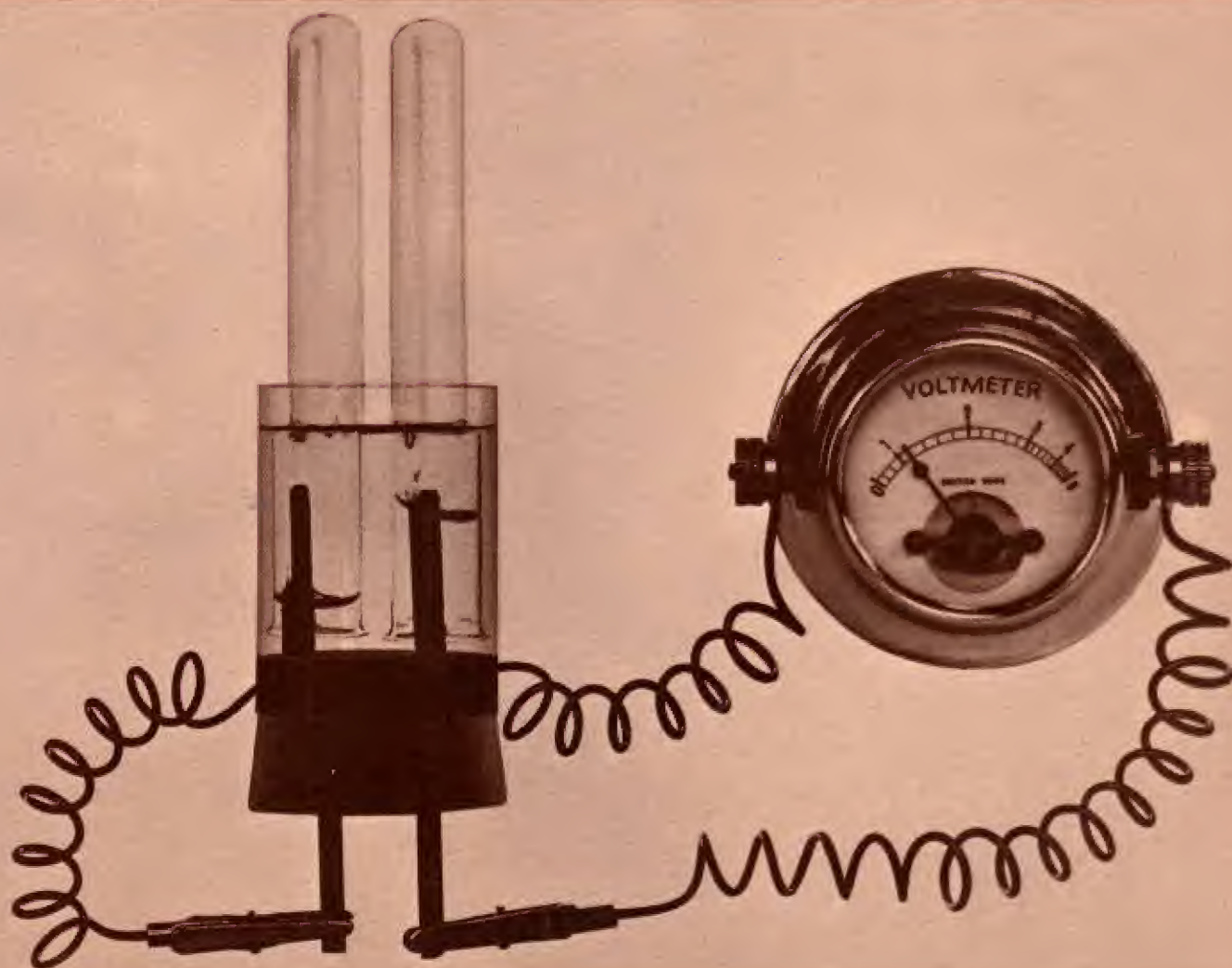


Chemistry and Electricity



INTRODUCTION

As you well know, when we want an ordinary torch battery to produce a current we join the two terminals of the battery with a wire or a torch bulb in order to complete a circuit. When the circuit is made, current flows, and the bulb lights. But even in the inactive battery the tendency for current to flow is present, waiting for the circuit to be completed. This tendency is known as 'electromotive force'. It is measured by the potential difference between the terminals of a cell when no current is being taken from it. The electromotive force is the ability of a source of electricity to set a current flowing once a suitable circuit is completed.

In any circuit the current flowing is determined partly by the electromotive force available. In general the higher the e.m.f., the larger the current. But a circuit also has a resistance, and the higher the resistance the smaller the current. These three factors are linked together:

$$\begin{aligned} \text{current (in amperes)} &= \frac{\text{e.m.f. (in volts)}}{\times \text{total resistance (in ohms)}} \\ \text{or} \quad \text{e.m.f.} &= \text{current} \times \text{resistance} \\ \text{volts} &= \text{amperes} \times \text{ohms} \end{aligned}$$

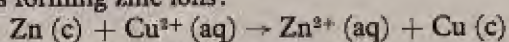
Electromotive force is something that a source of electricity has at all times. *Resistance* is something that a circuit has at all times. But a *current* is only obtained if a source of electricity is connected into a circuit.

PART I

ELECTRICITY FROM CHEMICALS

An electric current involves a flow of electrons. The chemical reactions which are useful in producing electricity are those which involve a transfer of electrons.

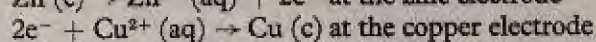
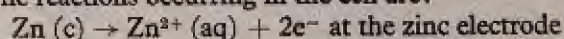
If zinc metal is put into copper sulphate solution, which contains copper ions, copper metal is produced and zinc dissolves forming zinc ions:



Two electrons have been transferred from zinc to copper, but this is a direct transfer in solution and not very useful. By separating the zinc and copper and making the electrons

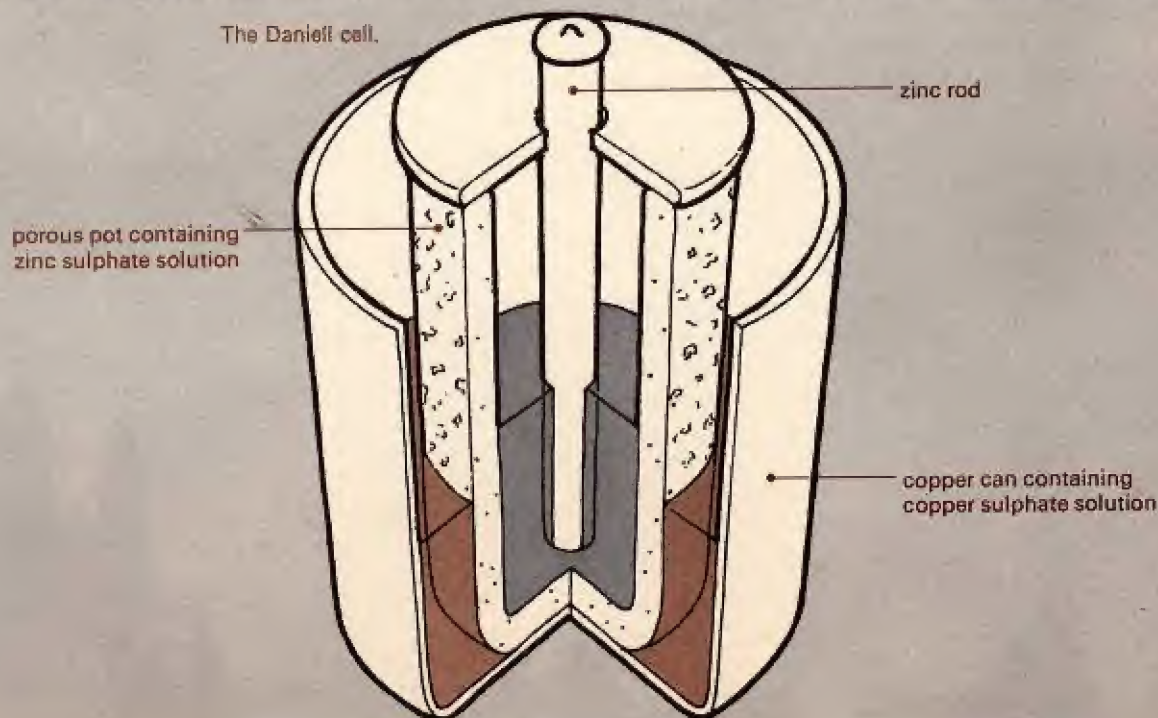
transfer through an outside circuit, a useful current is produced. The Daniell cell is a well-known means of doing this. It consists of zinc metal, zinc sulphate solution, copper sulphate solution, and copper metal. The two solutions are separated by a porous pot which allows them to make contact without mixing too freely.

The reactions occurring in the cell are:



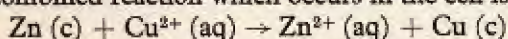
Surplus electrons are made available at the zinc. They flow

The Daniell cell.



from the zinc electrode through the outside circuit to the copper where they are used up. The conventional direction of current in the outside circuit is, however, from copper to zinc. This is because the conventions for describing electric currents were devised before the discovery of electrons. It was customary at that time to speak of a flow of current from the positive to the negative electrodes of a cell. When electrons were first postulated, it was realized that the negative electrode was negative precisely because surplus electrons were being made available to flow to the positive electrode. The result is that conventional descriptions of electric current indicate a current in the opposite direction to the flow of electrons. In the case of the zinc-copper cell, the electrons flow from zinc to copper, but the conventional direction of current is from copper to zinc.

The combined reaction which occurs in the cell is:

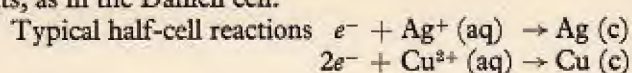


We say that the zinc is 'oxidized' to zinc ions and copper ions are 'reduced' to copper. In every oxidation-reduction reaction a material loses electrons and is said to be oxidized and another material gains electrons and is said to be reduced. The problem to be solved in producing useful electricity is how the oxidation and reduction components can be separated so that the electrons may be persuaded to transfer through an outside circuit.

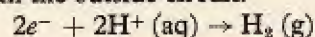
Electrodes and half-cell reactions – The Daniell cell may be set out in a very simple diagrammatic form so as to show clearly the two halves of the cell. Each half cell contains an electrode, consisting of a metal, and its corresponding ion in solution. The two electrodes here are zinc metal in a solution of zinc ions, and copper metal in a solution of copper ions. The reactions which occur at each electrode are known as *half-cell reactions*. By adding together the two half-cell reactions, we obtain the overall reaction occurring in the cell.

There are many kinds of electrodes. A few of the standard types are now described. The half-cell reactions are set out in each case as reductions. We shall describe these electrodes and half-cell reactions in some detail because we shall see examples of them in use throughout the book.

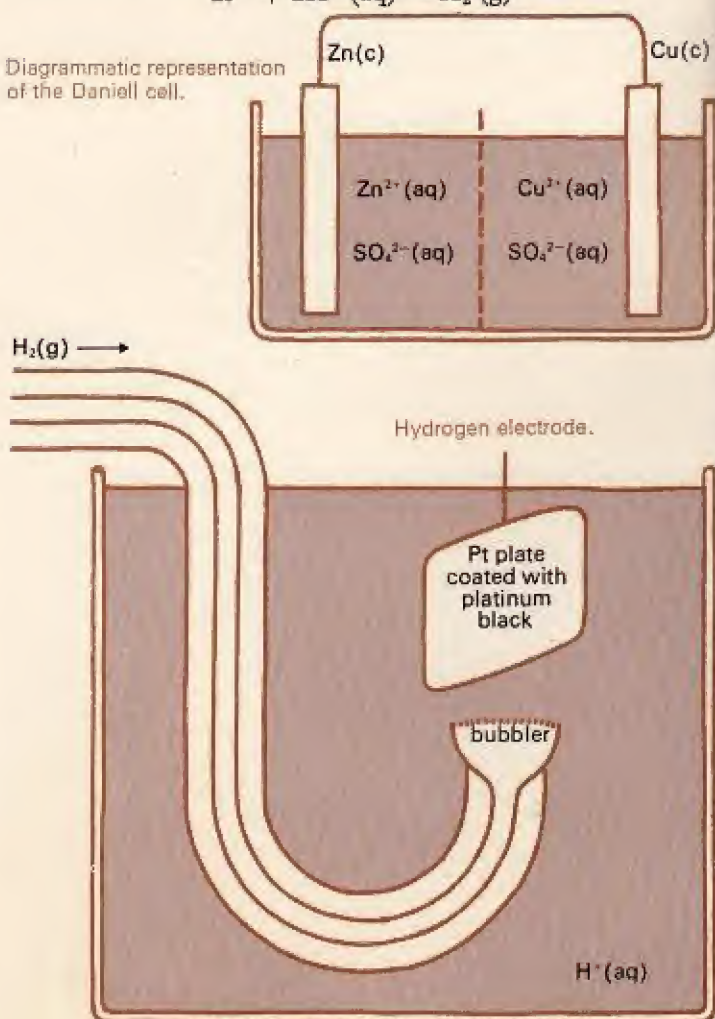
Metal electrodes – A metal dips into a solution of one of its salts, as in the Daniell cell.



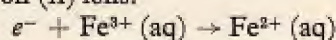
Hydrogen electrodes – Hydrogen gas is bubbled over a platinum plate in an acid solution. The platinum plate catalyses the equilibrium between the hydrogen ions in solution and the hydrogen gas. The platinum also serves as a terminal to make contact with the outside circuit.



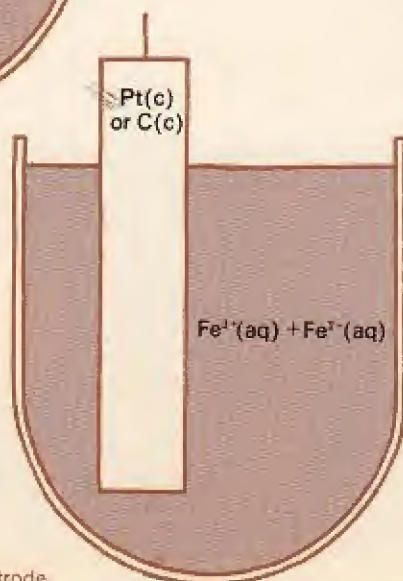
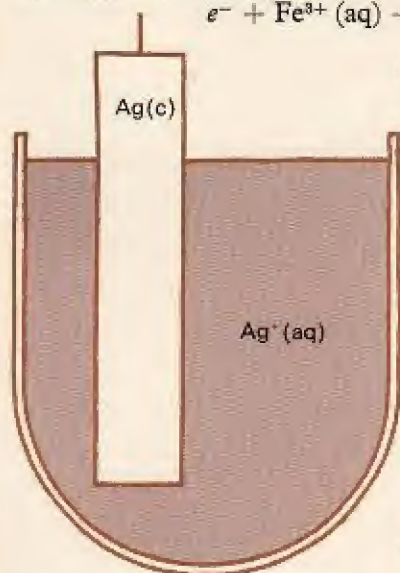
Diagrammatic representation of the Daniell cell.



Redox electrodes – All cells involve a reduction in one half cell and an oxidation in the other, so that all the electrodes we have described could be called redox (short for reduction-oxidation) electrodes. The name is normally reserved for the half cell which contains ions of a reduced and oxidized form in solution together. An unreactive conductor, such as platinum or carbon, dips into the solution and acts as a terminal for the outside connection. A very simple half cell of this type might consist of a platinum wire in a solution of both iron (III) and iron (II) ions.

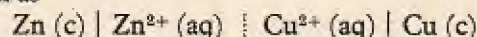


Metal electrode.



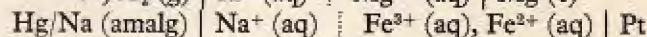
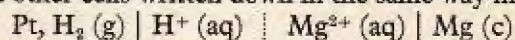
Redox electrode.

Making a complete cell – To make a complete cell we must combine two half cells. The method used in the Daniell cell has already been described. This cell is written down in shorthand form as



The solid vertical line represents the division between a solid and a solution. In the case of a hydrogen electrode, it represents the division between gas and solution. The broken line represents the division between the two liquids. In cells of this type the two liquids almost always meet in the pores of a porous non-reactive substance such as porous pot, porous plastic, string, paper, cloth, or glass wool, or at a very narrow opening which does not allow the solutions to mix freely. Solutions in two separate containers may be linked by an inverted U-tube containing a salt solution, each end plugged with paper or string; this is known as a salt bridge.

Some other cells written down in the same way might be:



Some cells can be set up with only one solution: for example



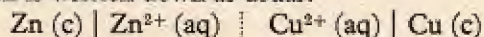
Both the chloride ions and the zinc ions required can be provided by a single solution of zinc chloride, without any need for a porous partition. This sort of cell has obvious practical advantages.

The righthand convention – Two half cells form a complete electrochemical cell. Until the outside circuit is completed, no current is delivered, but the *electromotive force* (e.m.f.) is present.

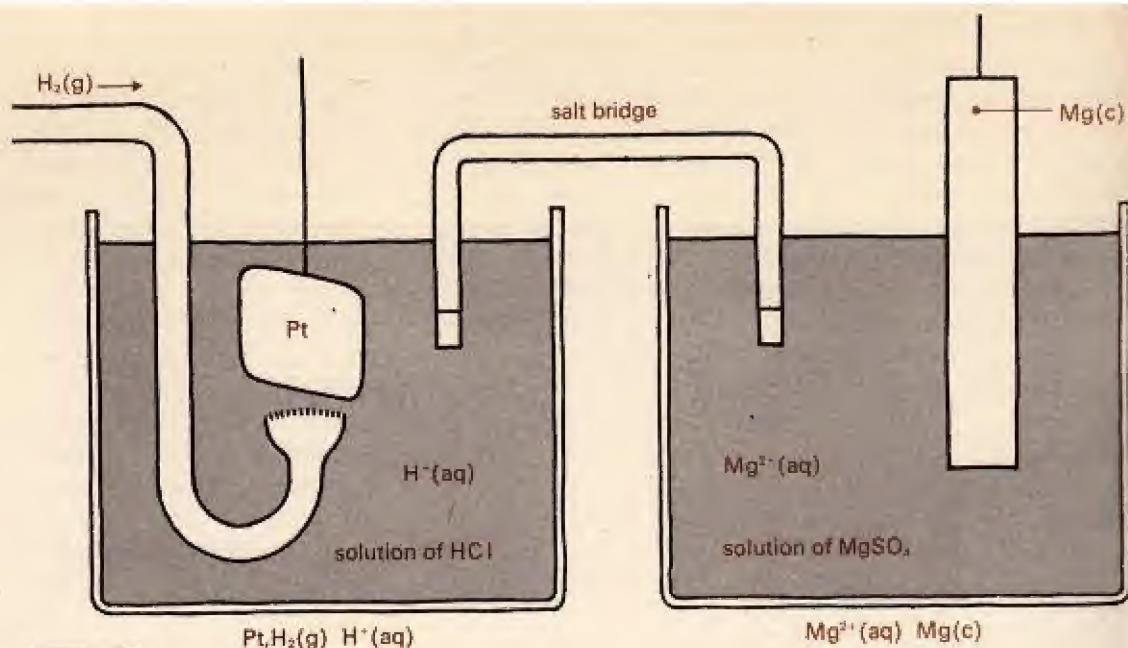
The e.m.f. of the cell is usually measured with a high resistance voltmeter or with a potentiometer. The current drawn from the cell while the measurement is being made is exceedingly small; the importance of this will be seen later (pp. 13-15).

When both solutions have a concentration of 1M, the potential of the Daniell cell, as measured in one of these ways, is found to be 1.1 volts. As it stands, however, this information is incomplete; it does not tell us in which direction a current will flow in an external circuit. We have another shorthand convention, the *righthand convention*, to enable us to include this information in the value given.

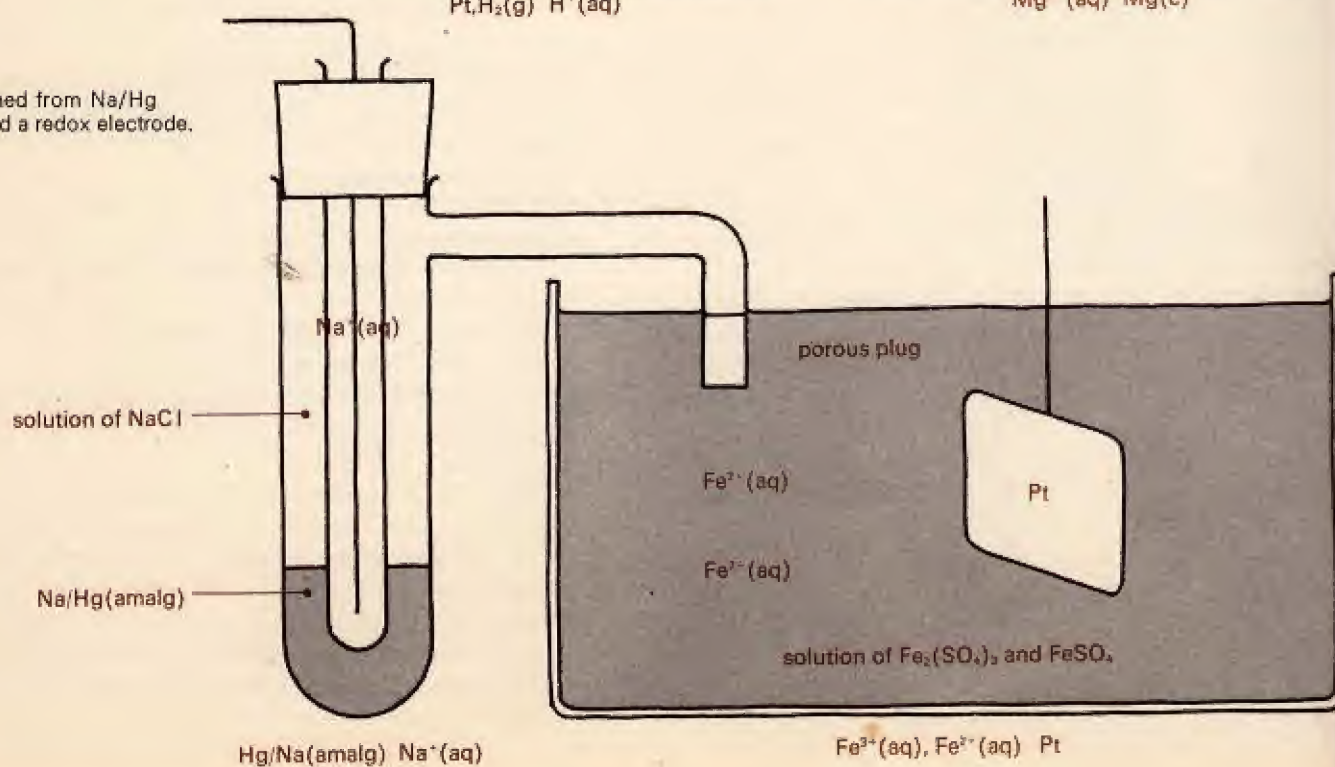
The cell is written down as usual:



a. Cell formed from a hydrogen electrode and a magnesium electrode.



b. Cell formed from Na/Hg electrode and a redox electrode.



If the conventional (as opposed to electron) *current* flow through the external circuit is *from right* to left, the potential of the cell is said to be positive.

The meter shows that this is the case for this cell; the current flows from the copper electrode through the external circuit to the zinc electrode. So $E = +1.1$ volts.

If we chose to write the cell arrangement in reverse; i.e.

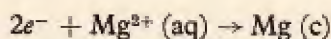


the current would still flow from the copper to the zinc in the external circuit, but it would no longer be from the right to the left of the diagram but from left to right. In this case the e.m.f. of the cell would be written as $E = -1.1$ volts.

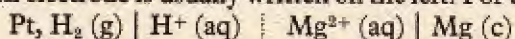
This is still the same cell, however, regardless of how it is written down. There is no physical difference between a positive and a negative e.m.f. These simply refer to the cell as written on paper. We cannot say that a cell has an e.m.f. of -1.5 volts. This is meaningless unless used to refer to a particular written description of the structure of the cell.

Summary – The sign of the e.m.f. of a cell depends on the way the cell diagram is written down. A +ve e.m.f. shows that the current flows through the external circuit from the righthand electrode. A –ve e.m.f. shows that the current flows through the external circuit from the lefthand electrode. The full statement of the cell e.m.f. must include the cell diagram.

Electrode potentials – The half-cell reactions we have mentioned have a different tendency to occur: in the case of one reaction

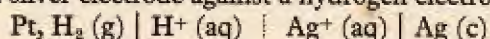


the tendency may be for the reaction to go from left to right or from right to left according to the nature of the other electrodes. Since we have no means of measuring individual tendencies or potentials they are all measured by comparison with the hydrogen electrode. In such comparisons, the hydrogen electrode is usually written on the left. For example,



In this case we find that the current does not tend to flow from right to left in the external circuit, but in the opposite direction. The e.m.f. of the cell is given a negative sign: $E = -2.38$ volts.

With a silver electrode against a hydrogen electrode,

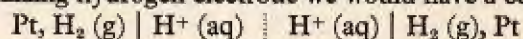


we find that the current does tend to flow from right to left in the external circuit so the e.m.f. is given a positive sign: $E = +0.80$ volts.

In the same way a complete list of single electrode potentials can be drawn up, all of them matched against the hydrogen electrode. (See chart on Page 7).

Since electrode potentials are affected by the concentration of the respective ions in the solution, all the electrode potentials given in the table refer to electrodes where the concentrations of ions are $1.00 \text{ g-ion litre}^{-1}$. These are called standard electrode potentials. All the values in the table are at 25°C .

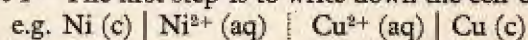
If we matched a second hydrogen electrode against the standardizing hydrogen electrode we would have a cell:



The two half cells balance one another and there is no tendency for current to flow in either direction. The cell e.m.f. is zero, as it would be for any cell composed of two identical half cells. The potential of the hydrogen electrode is arbitrarily taken as a standard of comparison for the others.

Working out the reaction in a cell

Example 1 – The first step is to write down the cell diagram,

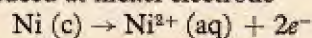


Then we must determine the e.m.f. of the cell. This may have to be done practically, which would mean setting up the cell, but we can often calculate the cell e.m.f. from the table of standard electrode potentials.

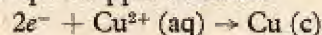
$$\begin{aligned} E_{\text{cell}} &= E_{\text{righthand electrode}} - E_{\text{lefthand electrode}} \\ &= +0.34 \text{ volts} - (-0.25 \text{ volts}) \\ &= +0.34 \text{ volts} + 0.25 \\ &= +0.59 \text{ volts} \end{aligned}$$

The cell e.m.f. has a positive sign so we know that the current flows in the external circuit from the righthand (copper) electrode to the lefthand (nickel) electrode. The flow of electrons in the circuit is in the opposite direction from the nickel to the copper. Excess electrons must be produced at the nickel electrode. They flow through the external circuit, and they are used up at the copper electrode. We can now write down the half-cell reactions which actually occur:

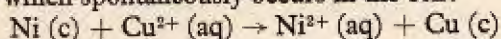
electrons produced at nickel electrode



electrons used up at copper electrode



By combining these two half-cell reactions we get the overall reaction which spontaneously occurs in the cell:



Example 2

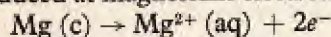


Work out the e.m.f. of the cell:

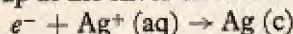
$$\begin{aligned} E_{\text{cell}} &= E_{\text{righthand electrode}} - E_{\text{lefthand electrode}} \\ &= -2.38 \text{ volts} - (0.80 \text{ volts}) \\ &= -3.18 \text{ volts} \end{aligned}$$

Since the cell e.m.f. has a negative sign, the current flows from left to right. So the electrons flow in the opposite direction, from right to left:

electrons produced at magnesium electrode



electrons used up at the silver electrode



In order to balance out the electrons the second half-cell reaction must be doubled before combining to give the overall reaction:



Cell potentials and how far a reaction should go – The calculations that we have just made are based upon standard electrode potentials, which only apply strictly when the concentrations of ions in solution are 1.00 g-ion litre⁻¹. In fact the electrode potential changes with concentration. This very important point is illustrated by the five graphs on this page and page 8.

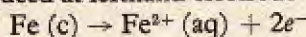
If we have a cell with initial concentration of both ions equal to 1.00 g-ion litre⁻¹:



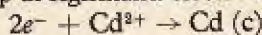
$$\begin{aligned} E_{\text{cell}} &= E_{\text{righthand electrode}} - E_{\text{lefthand electrode}} \\ &= -0.40 \text{ volts} - (-0.44 \text{ volts}) \\ &= +0.04 \text{ volts} \end{aligned}$$

The e.m.f. is positive. The current flows from right to left; electron flow is from left to right.

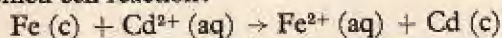
electrons produced at lefthand electrode



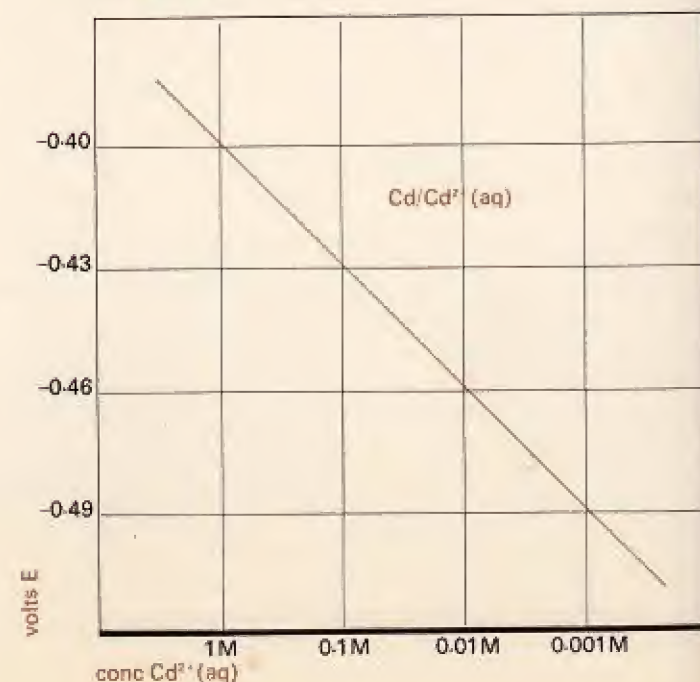
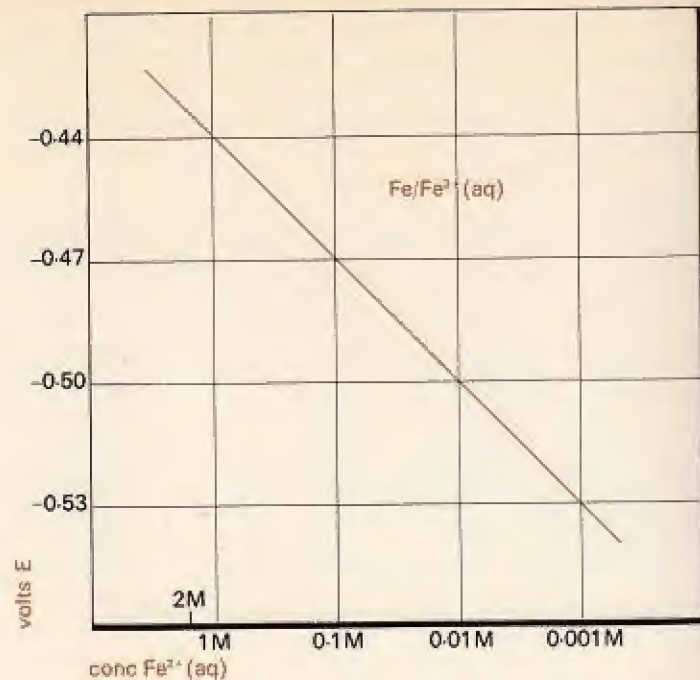
electrons used up at righthand electrode



Combined cell reaction:



If we let the reaction proceed spontaneously $\text{Cd}^{2+} (\text{aq})$ ions are removed from the solution, which gets progressively



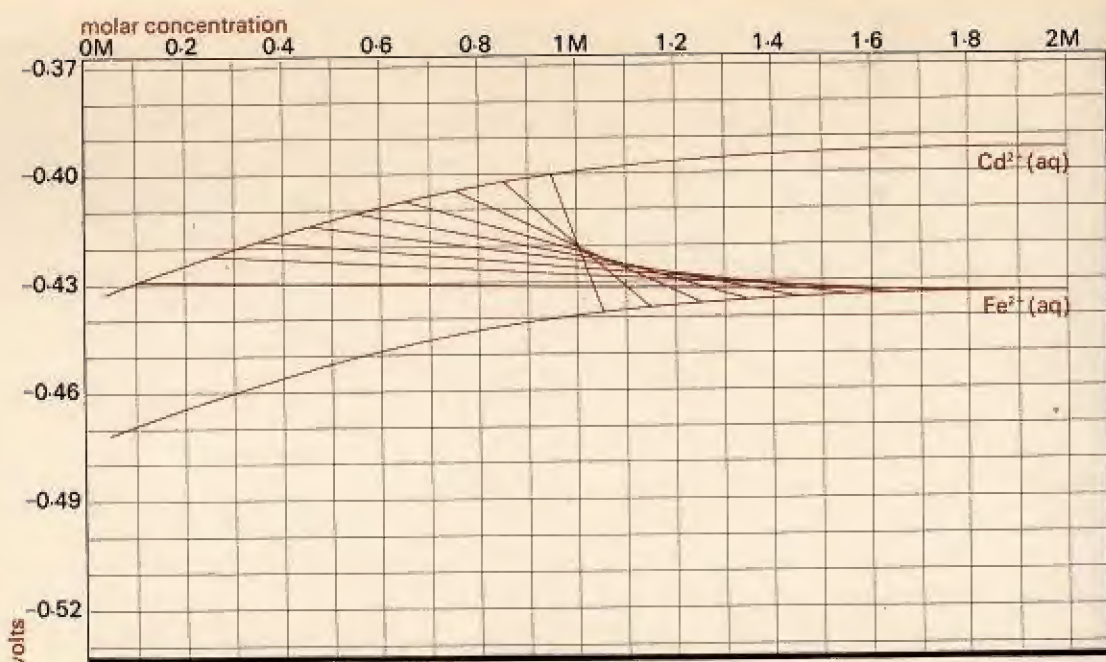
Graph (left) showing the variation of molar concentration with e.m.f. in an Fe/Fe²⁺ half cell.

Graph (left) showing the variation of molar concentration with e.m.f. in a Cd/Cd²⁺ half cell.

Pt, H₂ (g) | H⁺ (aq)

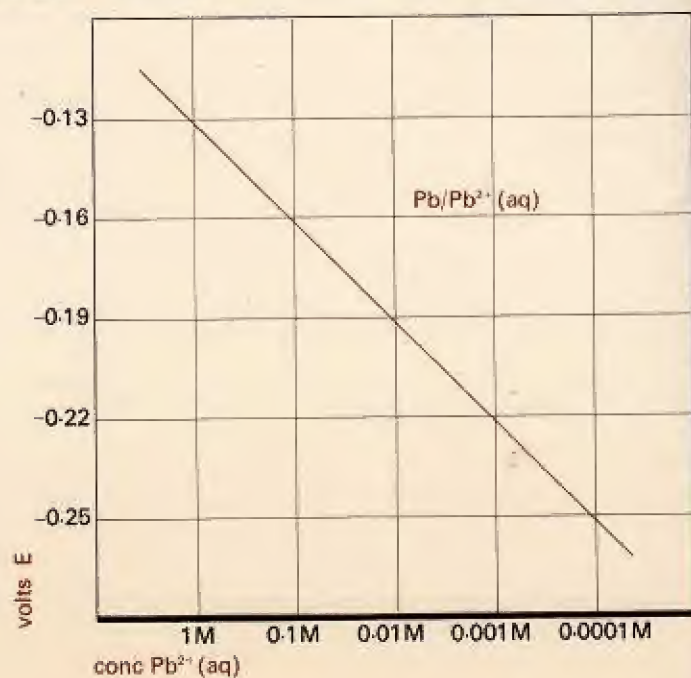
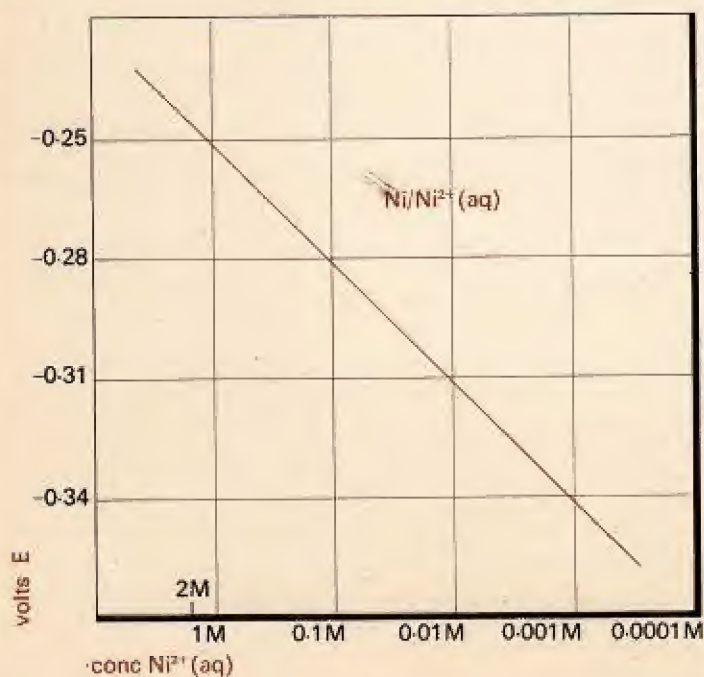
	<i>E</i> ⁰ volt
Mg ²⁺ (aq) Mg (c)	-2.37
Al ³⁺ (aq) Al (c)	-1.66
SO ₄ ²⁻ (aq) + H ₂ O (l), SO ₃ ²⁻ (aq) + 2OH ⁻ (aq) Pt	-0.93
Zn ²⁺ (aq) Zn (c)	-0.76
Fe(OH) ₃ (c), Fe(OH) ₂ (c) + OH ⁻ (aq) Pt	-0.56
Fe ²⁺ (aq) Fe (c)	-0.44
PbSO ₄ (c), SO ₄ ²⁻ (aq) Pb (c)	-0.30
Ni ²⁺ (aq) Ni (c)	-0.25
Pb ²⁺ (aq) Pb (c)	-0.13
H ⁺ (aq) H ₂ (g), Pt	0.00
SO ₄ ²⁻ (aq) + 4H ⁺ (aq), H ₂ SO ₃ (aq) + H ₂ O (l) Pt	+0.17
Cu ²⁺ (aq) Cu (c)	+0.34
I ₂ (in KI aq), 2I ⁻ (aq) Pt	+0.54
2H ⁺ (aq) + O ₂ (g), H ₂ O ₂ (aq) Pt	+0.68
Fe ³⁺ (aq), Fe ²⁺ (aq) Pt	+0.77
Ag ⁺ (aq) Ag (c)	+0.80
Br ₂ (aq), 2Br ⁻ (aq) Pt	+1.09
2IO ₃ ⁻ (aq) + 12H ⁺ (aq), I ₂ (aq) + 6H ₂ O (l) Pt	+1.19
MnO ₂ (c) + 4H ⁺ (aq), Mn ²⁺ (aq) + 2H ₂ O (l) Pt	+1.23
Cl ₂ (aq), 2Cl ⁻ (aq) Pt	+1.36
PbO ₂ (c) + 4H ⁺ (aq), Pb ²⁺ (aq) + 2H ₂ O (l) Pt	+1.46
MnO ₄ ⁻ (aq) + 8H ⁺ (aq), Mn ²⁺ (aq) + 4H ₂ O (l) Pt	+1.51
PbO ₂ (c) + SO ₄ ²⁻ (aq) + 4H ⁺ (aq), PbSO ₄ (c) + 2H ₂ O (l) Pt	+1.69
H ₂ O ₂ (aq) + 2H ⁺ (aq), 2H ₂ O (l) Pt	+1.17

Variation of molar concentration with voltages in $\text{Fe}^{2+} - \text{Cd}^{2+}$ cell.



Graph showing the variation of molar concentration with e.m.f. in a Ni/Ni^{2+} half cell. *Below.*

Graph showing the variation of molar concentration with e.m.f. in a Pb/Pb^{2+} half cell. *Bottom right.*



weaker, and an equal number of $\text{Fe}^{2+}(\text{aq})$ enter solution. When the concentration of cadmium ions in solution has fallen to 0.1 M, and the concentration of the iron ions has therefore risen to 1.9 M, we see that the electrode potentials of both electrodes have become about -0.43 volts. The e.m.f. of the cell is now:

$$\begin{aligned} E_{\text{cell}} &= E_{\text{righthand electrode}} - E_{\text{lefthand electrode}} \\ &= -0.43 \text{ volts} - (-0.43 \text{ volts}) \\ &= 0.00 \text{ volts} \end{aligned}$$

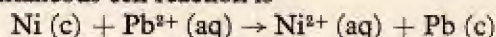
The cell e.m.f. is now zero, or in other words the cell is balanced, and there is no longer a tendency for the reaction to proceed spontaneously in any direction.

Let us take a second case involving lead and nickel electrodes.

The cell, again with ion concentrations of 1.00 g-ion litre⁻¹, is:

$$\begin{aligned} &\text{Ni (c)} \mid \text{Ni}^{2+}(\text{aq}) \parallel \text{Pb}^{2+}(\text{aq}) \mid \text{Pb (c)} \\ E_{\text{cell}} &= E_{\text{righthand electrode}} - E_{\text{lefthand electrode}} \\ &= -0.13 \text{ volts} - (-0.25 \text{ volts}) \\ &= +0.12 \text{ volts} \end{aligned}$$

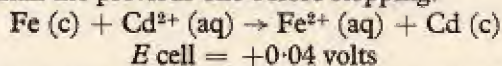
The spontaneous cell reaction is



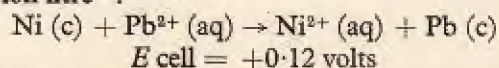
Lead ions are removed from solution and their concentration falls. When it has fallen to nearly 0.0001 M, $E = -0.24$ volts (righthand graph). The concentration of nickel ions rises but the potential only rises slowly (lefthand graph) and is now about -0.24 volts at 2 M concentration.

$$E_{\text{cell}} = -0.24 - (-0.24) = 0.00 \text{ volts}$$

So this reaction again has no tendency to go any further: it has reached equilibrium. Nevertheless it has gone much further than the previous one before stopping.



The reaction stops when $\text{Cd}^{2+}(\text{aq})$ concentration has fallen to 0.1 g-ion litre⁻¹.

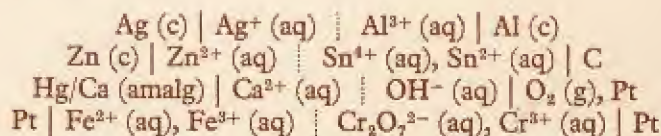


The reaction stops when $\text{Pb}^{2+}(\text{aq})$ concentration has fallen to 0.0001 g-ion litre⁻¹.

Summary

1. The sign of the e.m.f. of the cell as written indicates the direction in which the cell reaction will spontaneously tend to proceed.
2. The magnitude of the cell e.m.f. (ignoring the sign) gives us an indication of how far the reaction should proceed. A small e.m.f., e.g. 0.04 volts, indicates that the reaction will proceed to a slight extent, and a large e.m.f. that the reaction should go very close to completion.
3. In fact, as the reaction gets closer to its stopping point (or equilibrium point) it gets slower and slower and may take a very long time to reach this point. By a simple calculation we may avoid having to wait and see.
4. These are the main uses that a chemist makes of the e.m.f. of cells: deciding which way a reaction will go, and calculating how far it will go.

Question 1 Try to make quick sketches of the following cells, showing the solution to be used.



Question 2 See if you can work out how far the reaction in the cell

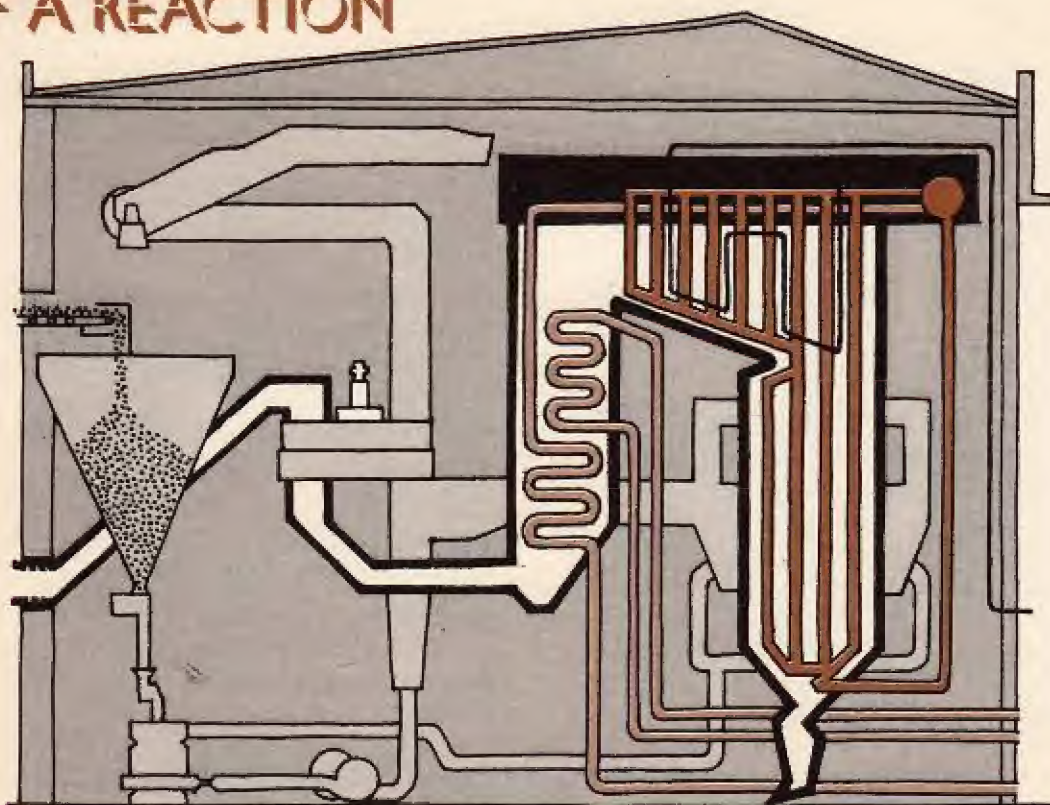
$\text{Cd (c)} \mid \text{Cd}^{2+}(\text{aq}) \parallel \text{Ni}^{2+}(\text{aq}) \mid \text{Ni (c)}$ should go before stopping. All the information you need is in the graphs we have already used.

PART 2

THE WORK OF A REACTION AND THE HEAT OF A REACTION

Diagram of boiler room of power station.

This electric express, capable of 100 miles an hour, is an example of the work produced by the chemical reaction taking place in the boiler room of the power station.
Photo. London Midland Region, British Rail.



The work done when 1 g-mol of electrons is moved through a potential difference of E volts is $1 \times E \times F$ joules, where F represents one faraday of electricity, the amount carried by a mole of electrons. When the units are changed to kcal, the amount of energy becomes $23 \times E$ kcal.

If we set up a cell with e.m.f. E volts, if the equation for the cell reaction involves the transfer of n electrons, and if we could move the electrons completely through the potential difference E while the reaction is taking place, then the total work obtained would be $23 \times n \times E$ kcal g-equation⁻¹. This

is called the work of a reaction, and is given the symbol ΔG .
$$\Delta G = -23 n E \text{ kcal g-equation}^{-1}$$

The negative sign is introduced because a cell which is generating electricity and doing work has 'lost' this energy from within itself; it is considered to be a negative quantity.

It would not be possible in practice to obtain and use all this work energy. One reason is that as the cell reaction proceeds concentrations change and the e.m.f. of the cell tends to fall. However, from the measured e.m.f. we are able to calculate the maximum theoretical work of a reaction ΔG .

Use of ΔG – The sign of ΔG can also be used to work out a spontaneous cell reaction. But ΔG values can be obtained in several ways, not only from cell e.m.f., so that they are even more useful than the latter. For any reaction



ΔG –ve indicates that the forward reaction (\rightarrow) is spontaneous.

ΔG +ve indicates that the reverse reaction (\leftarrow) is spontaneous.

Heat of a reaction – In an electrochemical cell the reactants are put together in a very special way in order to produce electricity. If these reactants are mixed in a beaker the same reaction may occur with the evolution of heat. We can measure

this heat of a reaction, and we give it the symbol ΔH . (If heat is evolved and 'lost' from the reactants ΔH is –ve, but if heat is absorbed or 'gained' ΔH is +ve.)

The Work of a reaction and the Heat of a reaction are not necessarily equal because in electrochemical cells some energy may be spent in the absorption or evolution of heat. Let us call this quantity Q kcal g-equation⁻¹ (+ve if heat is absorbed, –ve if heat is evolved). Now the total energy change in the cell must be the same as that in the reaction carried out in the beaker:

$$\Delta G + Q = \Delta H$$



PART 3

PRACTICAL CELLS FOR PRODUCING CURRENT

When cells are used for practical purposes three important factors have to be considered: the working voltage of the cell; the steady current it can deliver; and the total quantity of electricity it can deliver. The cost of the cell is another very important factor.

The working voltage - As we have seen, the e.m.f. E of a cell depends on the two electrodes. When the cell is used to deliver a current this e.m.f. E volts has to drive the current I amperes through the cell itself with internal resistance r ohms, as well

as through the external circuit, resistance R ohms.

e.m.f. = current multiplied by total resistance of circuit

$$E = I(R + r) = IR + Ir$$

The useful part of the e.m.f. is that which is used to drive the current through the external circuit, and this we call the working voltage.

Working voltage = current \times external resistance

$$\text{Working voltage} = IR$$

Hence $E = \text{working voltage} + Ir$. The working voltage is therefore always less than the e.m.f. of the cell.



Circuit indicating internal and external resistance.

Example 1

A cell: e.m.f. 1.644 volts. Internal resistance 0.3 ohms

External resistance	ohms	∞	32.6	11.4
Current drawn	amperes	0	0.05	0.14
Working voltage	volts	1.644	1.628	1.599

Example 2

A cell: e.m.f. 1.59 volts. Internal resistance 0.06 ohms

External resistance	ohms	∞	1.52	0.27	0.11
Current drawn	amperes	0	1.0	5.0	10.0
Working voltage	volts	1.59	1.52	1.33	1.10

The working voltage is only equal to the e.m.f. of the cell when the current drawn from the cell is zero. This is why we always measure a cell's e.m.f. with a high resistance voltmeter. The high resistance of the voltmeter, which is now the external circuit, only allows a minute current to pass so that the measured voltage is almost equal to the e.m.f. In the more accurate potentiometer method no current at all is drawn from the cell at the instant of measurement so that the full value is in fact recorded. This is sometimes called the 'open circuit voltage'.

In a practical cell the drop in e.m.f. is minimized by making the internal resistance as small as possible:

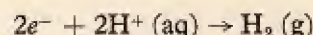
1. By making the electrodes as large as possible.
2. By putting the electrodes as close together as possible, but this is restricted by the need to enclose a reasonable quantity of reactive material between the electrodes.
3. By making the porous junction between the two electrolyte solutions as large as possible. If two solutions are only in contact at a single small junction, or if they are only joined by a strip of moist filter paper, although *this* may be sufficient for the e.m.f. to be measured, it presents a large resistance to any flow of current. It is far more satisfactory to have only one solution so that the liquid junction is eliminated.
4. By reducing the viscosity of the solutions so that ions can move freely. But for many purposes a 'dry' cell with the electrolyte in the form of a paste is desirable, so that it is not always possible to reduce the viscosity.

The steady current which a cell can deliver – As the resistance of the external circuit is decreased, the current drawn from

the cell increases. Working voltage = IR . If the working voltage is constant I increases as R decreases.

In effect more electrons are drawn through the external circuit with the result that the rate of electron transfer to and from the electrodes must increase. All the methods described for lowering the internal resistance of the cell will assist with this increase in current. There may now be other factors which limit the current which can be drawn from the cell; here are three examples:

1. If we have an electrode $\text{Pt}, \text{H}_2(\text{g}) \mid \text{H}^+(\text{aq})$ whose half-cell reaction is



bubbles of hydrogen collect on the platinum and hinder the following hydrogen ions from reaching the plate.

2. Electrode $\text{Pt} \mid \text{Fe}^{2+}(\text{aq}), \text{Fe}^{3+}(\text{aq})$
half-cell reaction $\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + e^-$

If a heavy current is drawn from the cell, the $\text{Fe}^{3+}(\text{aq})$ ions which are formed tend to accumulate at the platinum plate and hinder the access of further $\text{Fe}^{2+}(\text{aq})$ ions. At lower currents the ions which are formed diffuse away from the plates and there is no problem.

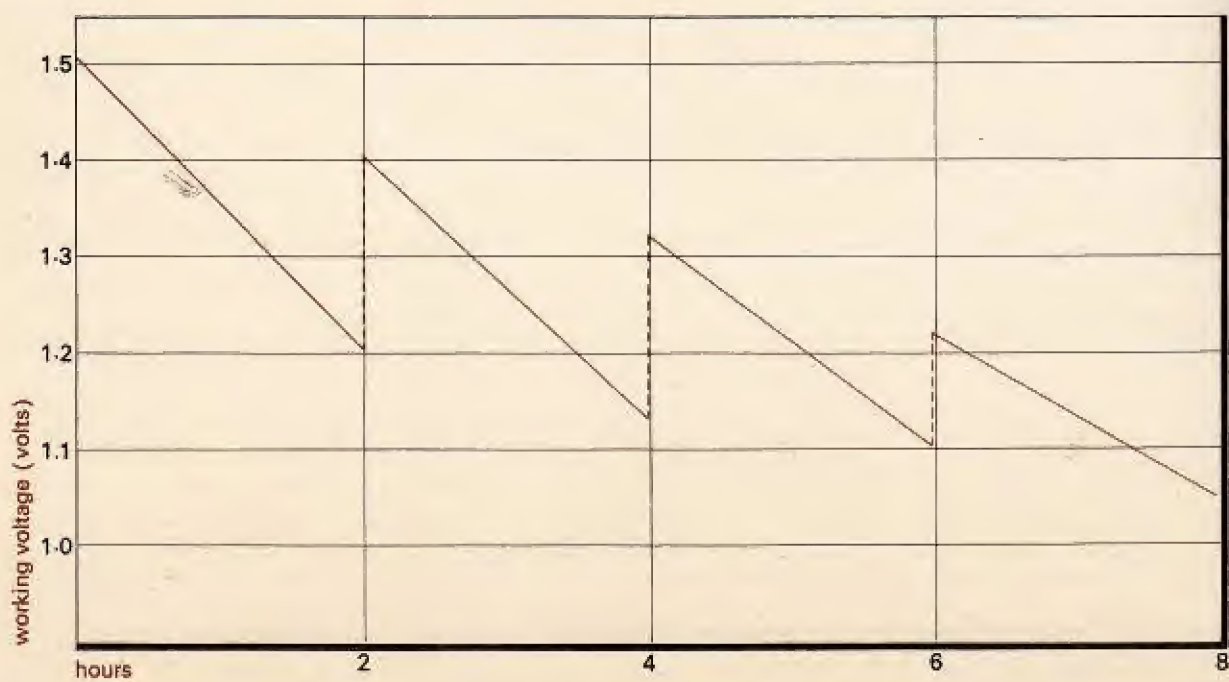
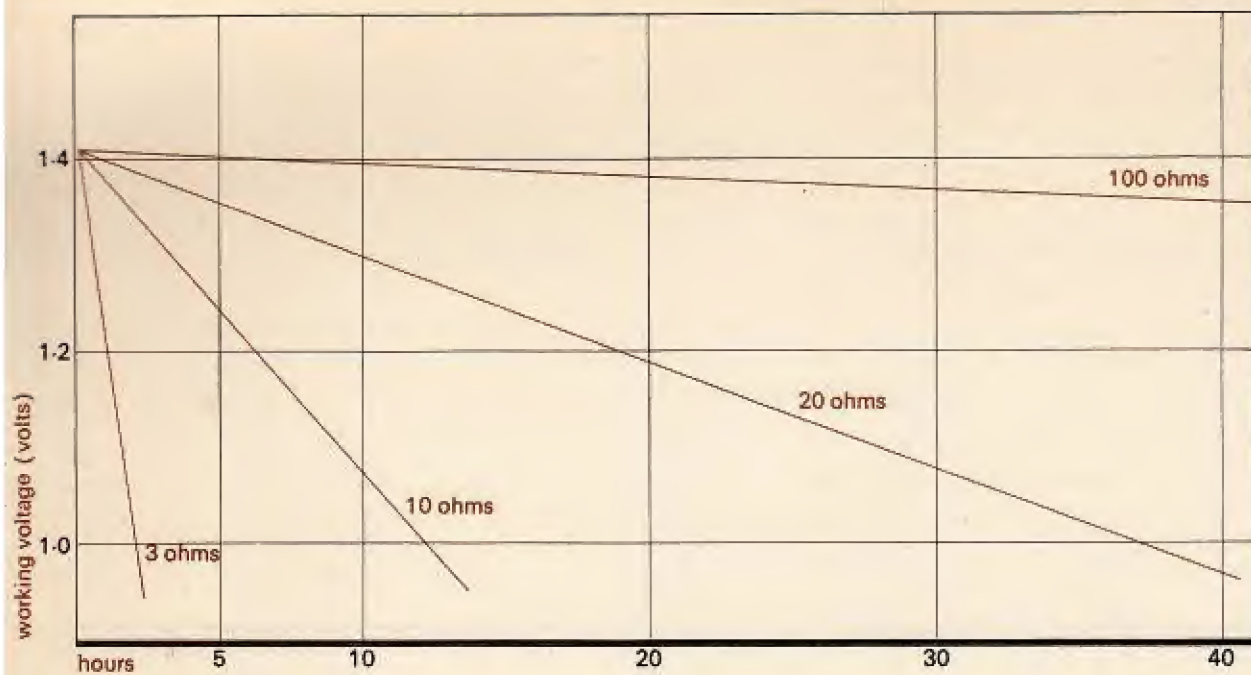
3. Electrode $\text{Cu}(\text{s}) \mid \text{Cu}^{2+}(\text{aq})$
half-cell reaction $2e^- + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Cu}(\text{s})$

If a heavy current is drawn, the $\text{Cu}^{2+}(\text{aq})$ ions nearest the metal are discharged. There may be a time lag before further ions can move up to take their place.

All these effects are known as 'polarization effects'. They all tend to limit the current which can be drawn from any cell. As a cell becomes polarized it becomes incapable of delivering the required current. This shows up in practice as an increased internal resistance and a fall in the working voltage of the cell.

A cell with large electrodes provides plenty of surface for electron transfer to occur so that heavy currents may be drawn from it before polarization sets in: in a smaller cell with small electrodes polarization may occur at much smaller currents.

The total quantity of electricity a cell can deliver – The total quantity of electricity depends primarily on the amount of reactive material in the cell. Theoretically, 2 gram equations of material should deliver twice as much electricity as 1 gram equation. In practice, not all the reactive material in a cell



is used up. As concentrations fall and polarization sets in, the working voltage falls and the cell has to be discarded. If a cell is to be used only once it is obviously desirable that it should be designed to use up as much of the reactive materials as possible.

If a heavy current is drawn continuously from a cell, polarization sets in quickly and the quantity of electricity obtained is much less than that which is theoretically possible. Very small currents do not have the same tendency to cause polarization. By taking a small current only over a longer period of time, a quantity much closer to the theoretical maximum is obtained.

Example – Four similar cells, of initial working voltage 1.4 volts were discharged through resistances of 3, 10, 20, and 100 ohms. With this type of cell the working voltage falls continuously in use and they are considered to be used up when the working voltage has fallen to 1 volt. The following observations were made:

Resistance R ohms	3	10	20	100
Time t hours for working volts to fall to 1 volt	2.1	12	37	310

During discharge from 1.4 volts to 1.0 volts the average working voltage is 1.2 volts, so we can calculate the average current in each case. This is given in amperes by $1.2 \text{ volts}/R \text{ ohms}$. The total quantity of electricity obtained in each case is given in amp-hours by *average current multiplied by time to fall to 1 volt*.

Resistance R ohms	3	10	20	100
Time t hours	2.1	12	37	310
Average voltage volts	1.2	1.2	1.2	1.2
Average current amperes	0.4	0.12	0.06	0.012
Quantity of electricity amp-hours	0.84	1.44	2.22	3.72

Intermittent use – If a cell is not used continuously its active working life can be much longer. When a cell is used for a short time, then rested, then used again and rested, and so on, the graph of the working voltage is as given opposite.

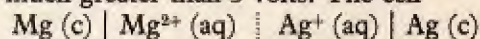
The broken vertical lines on the graph correspond to the resting periods and indicate that the cell recovers part of its lost working voltage during these periods. This is because the materials which polarize the cell have time to diffuse away

from the electrodes. Warming the cell assists this process by making it easier for the diffusion to take place; this is why a torch battery, or a transistor radio battery, which appears to be quite dead can be revived by letting it stand in front of the fire. Eventually of course a point will be reached where the cell can no longer be revived because all the reactive material has been used up.

The difference which intermittent use makes is illustrated by the following results. Three 1.5 volt torch cells were discharged through 4 ohm resistances (about the resistance of a small torch bulb), in three different ways. The working time of each was recorded until the working voltage had fallen to 0.9 volts.

1. Discharged for 4 minutes at the beginning of each hour, for 8 hours per day. Working time to 0.9 volts = 697 minutes.
2. Discharged for 4 minutes at the beginning of each quarter hour for 8 hours per day. Working time to 0.9 volts = 588 minutes.
3. Discharged continuously. Working time to 0.9 volts = 210 minutes.

Cells and batteries – The e.m.f. and working voltage of a single cell are limited by the electrode potentials and can hardly be much greater than 3 volts. The cell



has an e.m.f. $E = 3.18$ volts, but 1 to 2 volts is more common in practice.

A higher e.m.f. is easily obtained, however, by connecting a number of individual cells in series. The total e.m.f. is the sum of the individual e.m.f. of the cells.

The symbol for a single cell is $---| |---$. Here the longer vertical stroke represents the positive terminal. A number of cells connected in series is represented by $---| | | | | | | |---$.

Such a collection of cells is referred to as a 'battery'. In everyday language we may talk of a 'dry battery' or a 'torch battery' which may in fact consist of a single cell.

If a number of identical single cells are connected in parallel, we have a second type of *battery*. The combined potential is equal to the potential of the single cell. The advantage of this battery is that it may have a longer life and deliver heavier currents than one cell alone.

PART 4

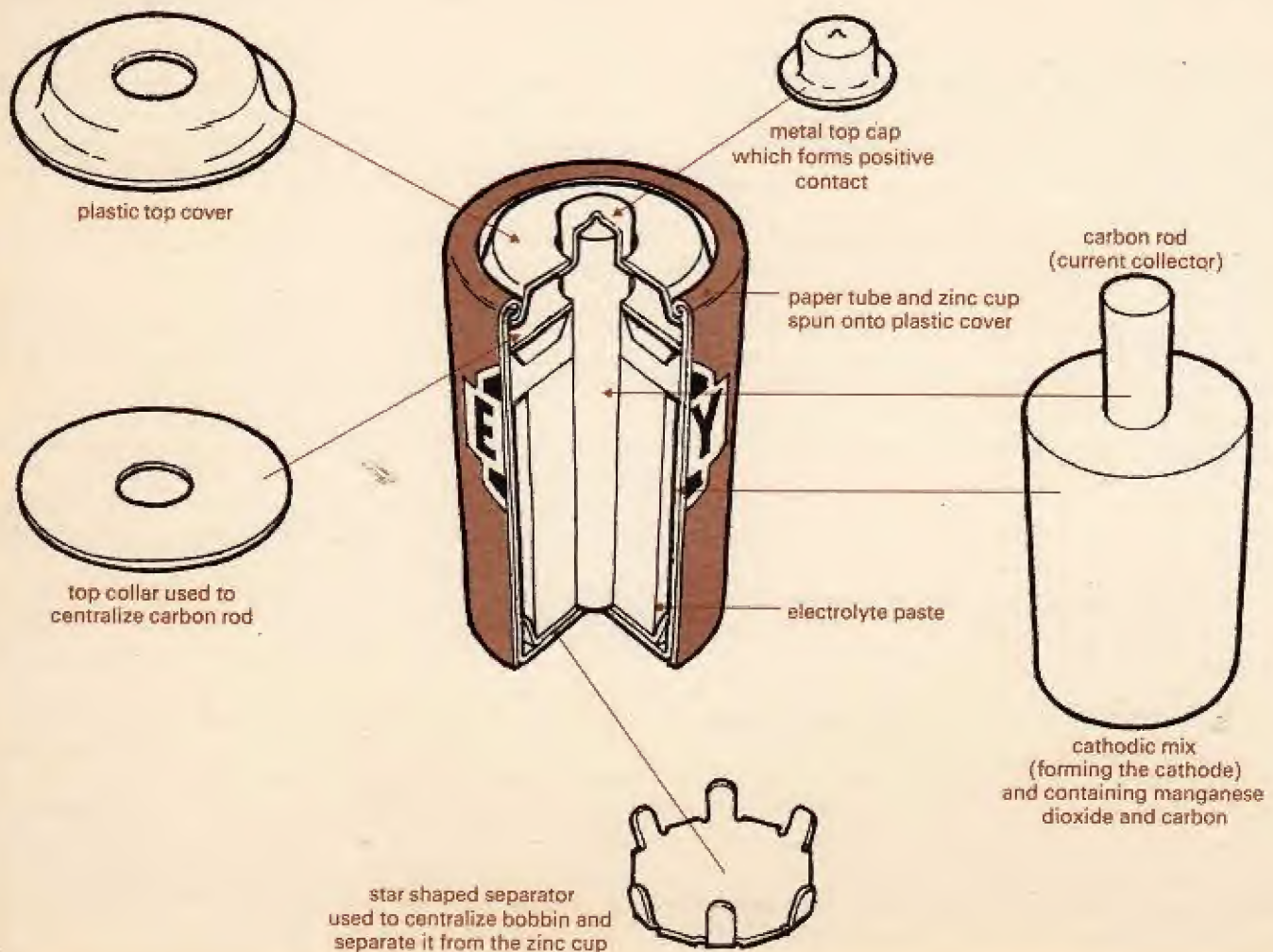
MODERN CELLS IN EVERYDAY USE

Two dry cells

a. Leclanché cell.

The commonest electrochemical cells in use today are dry cells and batteries, and the lead accumulator or car battery. We shall examine the lead accumulator in a moment. For now, let us pay attention to the dry cell and other cells of the same type.

The ordinary dry cell has been produced commercially since the end of the nineteenth century, with very little change. It was originally a modification of a cell devised by Georges Leclanché. It is sometimes still referred to as the 'dry Leclanché cell'. He was experimenting with electrochemical



electrolyte solutions, different mixtures of manganese dioxide and carbon, and so on, but these were the components of his completed cell. His description of the cell was published in 1868.

The only other step required to produce a dry or unspillable cell was to immobilize the ammonium chloride solution, and this was soon achieved by making it into a moist paste. Gassner in 1888 used a zinc cylinder as an outer casing and as electrode, giving us the prototype dry cell as we know it.

The modern cylindrical dry cell consists of:

- a. The carbon rod with a brass cap.
- b. The 'bobbin' consisting of 60 per cent manganese dioxide, 20 per cent carbon black, 10 per cent ammonium chloride, 10 per cent water, held together in a muslin bag.
- c. The paste electrolyte, consisting of 26 per cent ammonium chloride, 9 per cent zinc chloride in water which has been made into a paste with flour and starch. This is packed between the bobbin and the outer can. Some forms of high power cells have thin paper separators soaked in electrolyte, instead of a wall of paste.
- d. The zinc can, usually alloyed with 0.3 per cent lead and 0.3 per cent cadmium. The open end of the can is sealed with pitch.
- e. (Not shown on diagram.) The cardboard outer wrapping. Some cells are coated with pitch and encased in a steel jacket if external corrosion is likely.

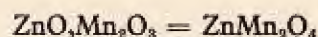
Many sizes of cylindrical cells are produced containing increasing amounts of reactive material. The voltage of each of these cells is about 1.5 volts, although differences in manufacture may cause variations between about 1.5 and 1.65 volts.

Flat, rectangular dry cells are used to build up batteries to give greater potentials; they have the same components:

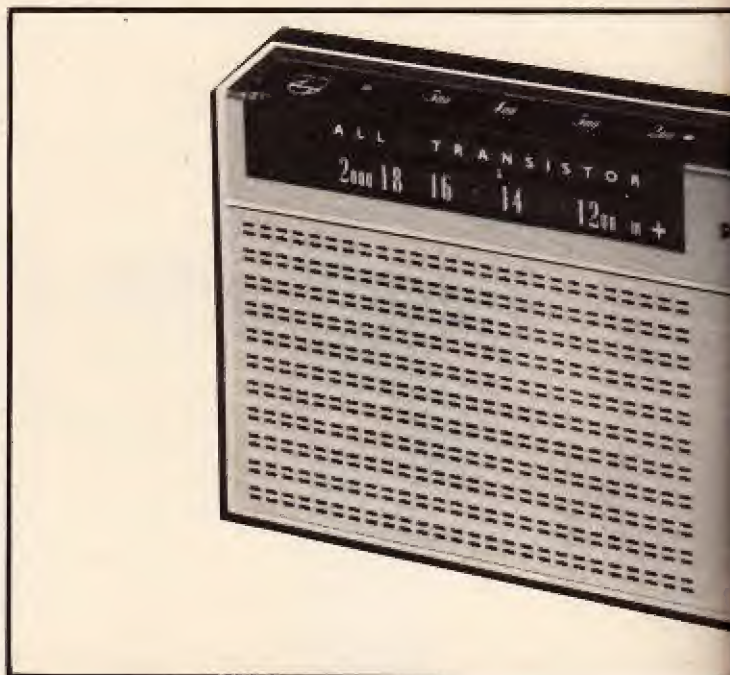
- a. A layer of carbon.
 - b. A flat pellet of manganese dioxide mixture.
 - c. Paper impregnated with electrolyte, separating the manganese dioxide and the zinc.
 - d. Zinc plate.
 - e. Plastic edge wrapping to prevent short circuits.
- These flat cells are conveniently built up in compact stacks, with the zinc plates and carbon layer back to back. Each flat cell adds 1.5 volts to the potential of the stack so that batteries with any desired potential are easily manufactured.

Chemistry of the dry cell – Even though it has been in use for over seventy years, the chemical reactions occurring in the cell are hardly yet understood.

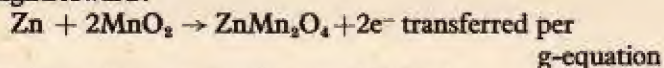
Analysis by X-ray diffraction has shown that when small currents are drawn from the cell, a material is formed which is identical with the mineral hetaerolite, which has the structure



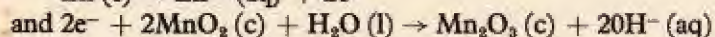
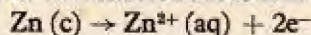
Working back from here, we need to find two electrode reactions (or half-cell reactions) which could result in this



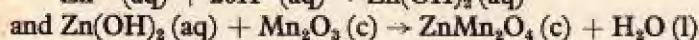
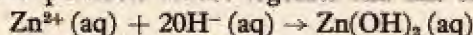
product. As an overall reaction this seems to be quite straightforward:



The two electrode reactions could then be



The products diffuse together and this ensues:



We must stress that these reactions are purely speculative; all we can really say is that they lead to the known final product.

But the problem is by no means solved, especially since other products are found in the cell when heavier currents are drawn from it.

The zinc chloride which is included in the electrolyte appears to have many functions. It causes the starch-flour paste to set to a jelly after the cell has been put together; it lessens the possibility that the zinc may corrode while the cell



A few uses of dry cells:

Portable radios.

Philips.

Torch lights.

Ever Ready.

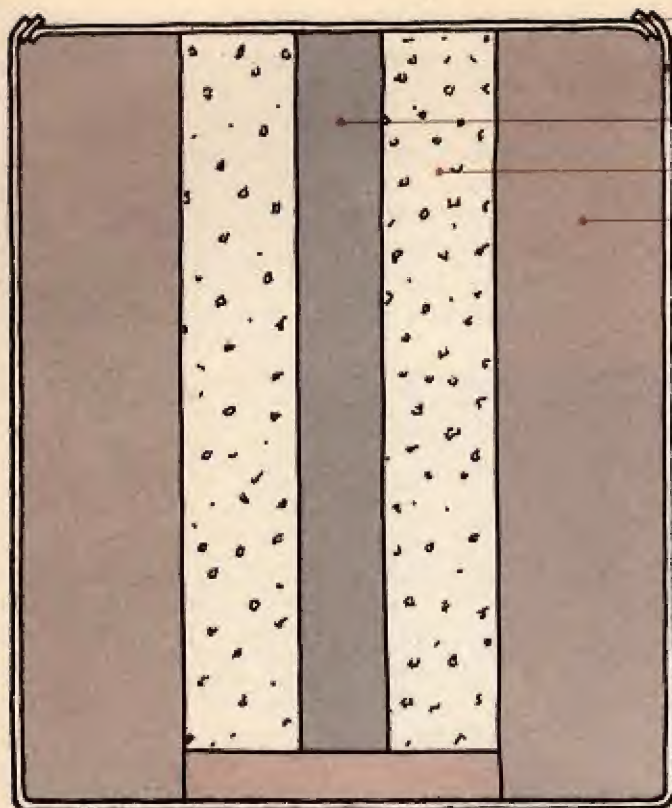
Heart pacers: this tiny electric cell is implanted in the region of the heart and regulates the heart-beat electrically.

Devices Implants Ltd.

Hearing aids.

Philips.

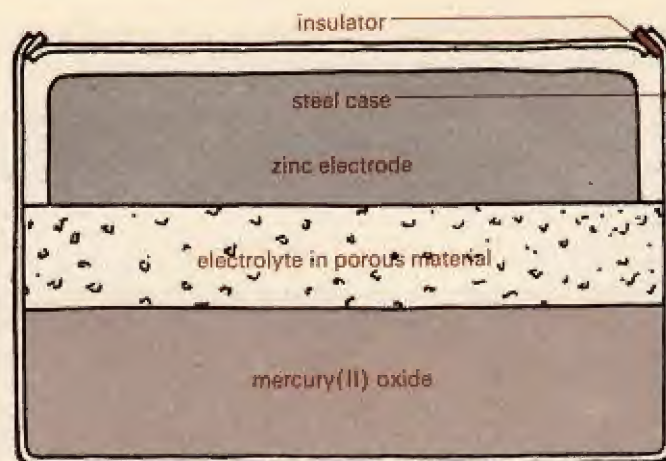




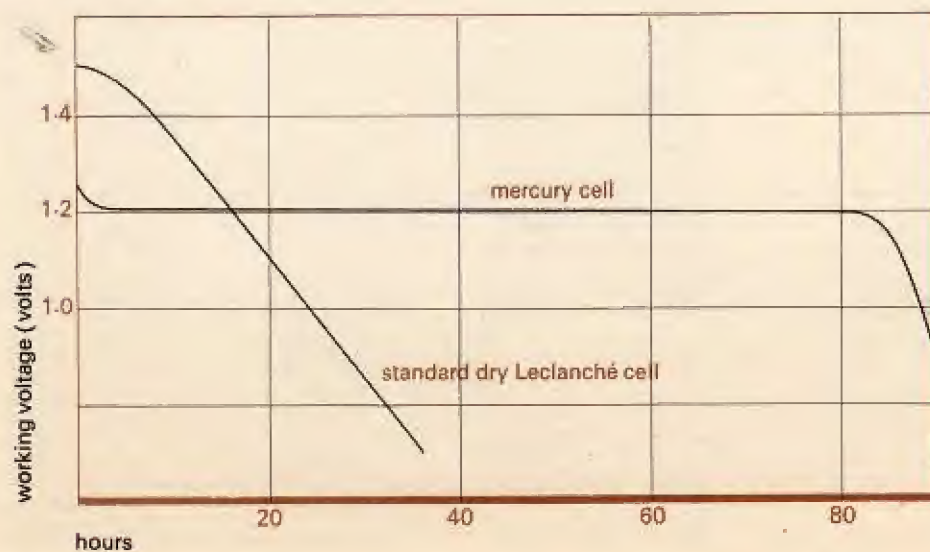
upright cell

- insulator
- steel case
- zinc electrode
- electrolyte in porous material
- mercury(II) oxide

The upright cylindrical and button mercury cells.



button cell



Graph showing the performance of a small mercury cell discharging through 10 ohms resistance.

is not in use; and it is also hygroscopic (moisture absorbing) so that it helps to keep the cell from drying out during storage. However, if the zinc can should become perforated, as it may well do towards the end of its useful life, this hygroscopic action causes the mixture to absorb much moisture from the atmosphere and corrosion proceeds rapidly. This is why old batteries should never be left in torches or cycle lamps or in any electrical equipment.

Alkaline dry cells (also known as manganese alkaline cells) – These cells, which are a comparatively recent development, are claimed to deliver a much greater quantity of electricity than the standard dry Leclanché cell of the same size, especially if used continuously.

They are constructed with a zinc cylinder at the centre surrounded by manganese dioxide-carbon mixture, so that they are similar to the standard dry Leclanché cell but inside out. The electrolyte is an alkaline solution of 30 per cent sodium hydroxide (in the dry Leclanché the ammonium chloride paste is slightly acid), but the e.m.f. of the cell is again about 1.5 volts, which suggests that the reactions in these two cells may be similar.

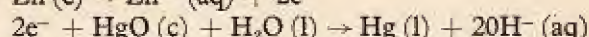
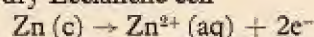
Since the manganese dioxide now forms the whole of the outside surface of the cell instead of the single carbon rod at the centre of the Leclanché cell, the manganese dioxide electrode covers a much larger terminal area, which may assist in reducing polarization. Reducing polarization allows more complete use of reactive material and a longer working life when the cell is in continuous use.

Though the cells are more expensive than standard cells of equal e.m.f., they are useful where continuous use or infrequent battery changing is required and where the current required is fairly heavy, say up to 0.5 ampere. They are used in portable television sets, record players, tape recorders, electric motors, electric shavers, and photoflash equipment.

Mercury cells or Ruben Mallory cells – Another cell which is now on sale in this country is the mercury cell. It was devised by Samuel Ruben and developed by the Mallory Company, and is often referred to as the Ruben Mallory or RM cell.

In principle the cell is similar to the dry Leclanché cell in that it has a zinc electrode and an oxide electrode, mercury (II) oxide in this case. The electrolyte is a concentrated solution of potassium hydroxide and zinc oxide in water.

The electrode reactions are (probably) simpler than those of the dry Leclanché cell



overall $\text{Zn (c)} + \text{HgO (c)} + \text{H}_2\text{O (l)} \rightarrow \text{Zn(OH)}_2 \text{ (aq)} + \text{Hg (l)}$
The e.m.f. of the cell is close to 1.35 volts.

The construction of the cell is also quite straightforward as seen in the diagrams of the upright cylindrical and the button cells. A little graphite is mixed with the mercury(II) oxide to improve its initial conductance.

Some of the exceptional characteristics of the mercury cell are:

a. Stability. The zinc oxide dissolved in the potassium hydroxide solution makes the zinc electrode less subject to internal attack. The cell is enclosed in steel so that there is no possibility of internal deterioration. As a result the cells may stand for long periods without use. The cells are also suitable as standards of voltage – the e.m.f. of the cell is very constant over short periods of use and remains so for years.

b. Constant voltage during discharge. Unlike the dry Leclanché cell, the working voltage remains constant at moderately low currents. The reason for this is that polarization does not occur in the same way. As mercury(II) oxide is reduced to metallic mercury, the flow of current in the cell is promoted rather than hindered, because mercury is such a good conductor.

c. The efficient use of material. Zinc hydroxide, which is the other reaction product, dissolves in the potassium hydroxide electrolyte. Thus there are no products to polarize or 'block' the cell, and about 90 per cent of the active material can be used for current production. For this reason, the efficiency of the cell per unit volume is high. Example: 6 cm × 3 cm (diameter) cells discharged at 0.25 amperes

Manganese alkaline	10 ampere-hours
Mercury cell	14 ampere-hours

(A standard dry Leclanché cell would not be suitable for discharging at this current, and would polarize very quickly, giving, say, at best 4 ampere-hours.)

d. Size. Another effect of this high efficiency is that the size of the mercury cell with its simple construction may be reduced very considerably. The smallest cell listed in the Mallory catalogue at present is 7.75 mm diameter and 4.43 mm high, volume 0.16 cm³. This has a capacity of 35 milliampere-

hours and a maximum current drain of 5 milliamperes. Such miniature cells have many uses, several of them medical. Hearing aids can be made invisible because there is no need for a cord to connect them to a large battery: the 'radio pill' has been developed which is swallowed by the patient and transmits information to the doctor; and 'pacemakers' to maintain a regular heart-beat have been stitched inside patients, all powered by miniature cells.

e. Robustness and versatility. Mercury cells can operate over a wider range of temperatures than other cells. Low temperature cells have been developed which deliver appreciable currents at -20°C , and some current even at -54°C .

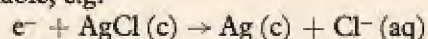
All these advantages have to be set against the high cost of these cells, which is inevitable because of the high cost of mercury and mercury compounds.

Indium/bismuth and silver oxide cells – These are two more cells of the same basic type which are produced in this country at present. The indium/bismuth cell is similar to the mercury cell except that an electrode of indium-bismuth alloy replaces the zinc electrode, and the electrolyte is 50 per cent aqueous potassium hydroxide solution saturated with indium hydroxide. The cell is especially designed for low temperature work, and at -25°C will deliver 40 per cent of its full room temperature capacity. Its e.m.f. is 1.16 volts.

The electrodes of the silver oxide cell are zinc and either silver (I) oxide (Ag_2O) or silver(II) oxide (Ag_2O_2). The electrolyte is aqueous potassium hydroxide solution.

These cells have a constant working voltage of about 1.5 volts. They deliver a large quantity of electricity in relation to their weight (about the same as the manganese alkaline cells) and are especially suitable for applications in which large currents are called for.

Silver chloride cells – All the cells that we have described so far have had electrodes of insoluble oxide which is reduced in the course of the cell reaction. An insoluble chloride is equally suitable, e.g.



One use of this electrode is in dry storage cells. This type is stored without electrolyte and may have, for example, a magnesium electrode to make up the cell. In emergency use at sea, for example, the cell is filled with sea water:

$\text{Mg}(\text{s}) \mid \text{Na}^+(\text{aq}), \text{Cl}^-(\text{aq}) \mid \text{AgCl}(\text{s})$, metal terminal and becomes active immediately on immersion. The cells are well suited to this purpose because:

- Magnesium has a high electrode potential. Its working voltage = 1.5 volts.
- Its atomic weight is low so that 26 g are electrochemically equivalent to 65 g zinc.
- Its density is low so that the small weight required will make a large electrode.
- Silver chloride is reduced to silver in the course of the reaction; this increases the conductance of the cell and assists in maintaining a steady voltage.
- For the same reason, fairly large constant currents can be drawn from the cell to maintain a signal light, and the bulk of the electrode materials are used up before the cell ceases to function.
- Salt water is an ideal electrolyte, but fresh water will also activate the cells.
- The cells will work even in freezing water.

Copper (I) chloride can be used as an alternative to silver chloride. It is much less expensive, but is less effective in cold water.

PART 5

STORAGE CELLS

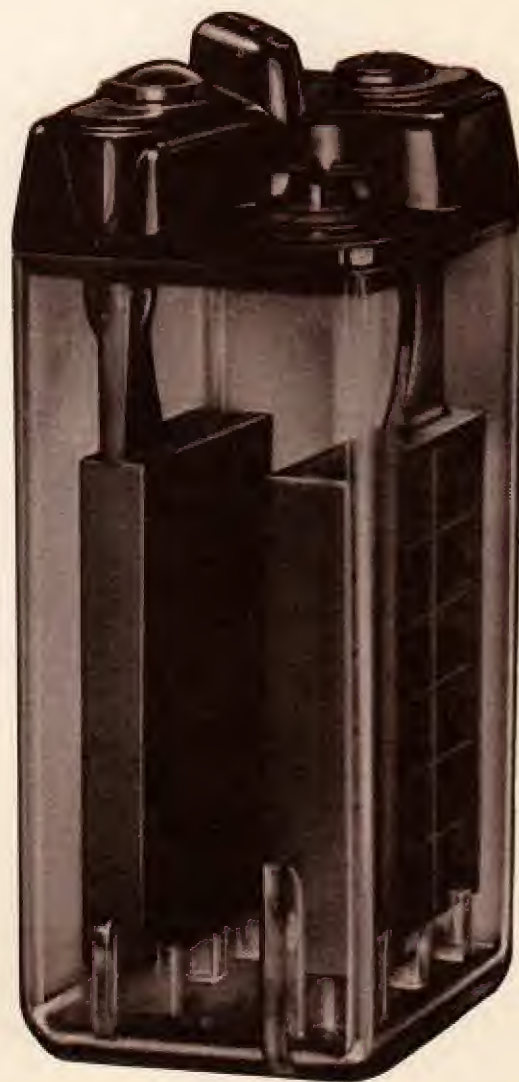
Lead-acid cell of simple construction of one positive and one negative plate in a Polystyrene container.
Electric Power Storage Ltd.

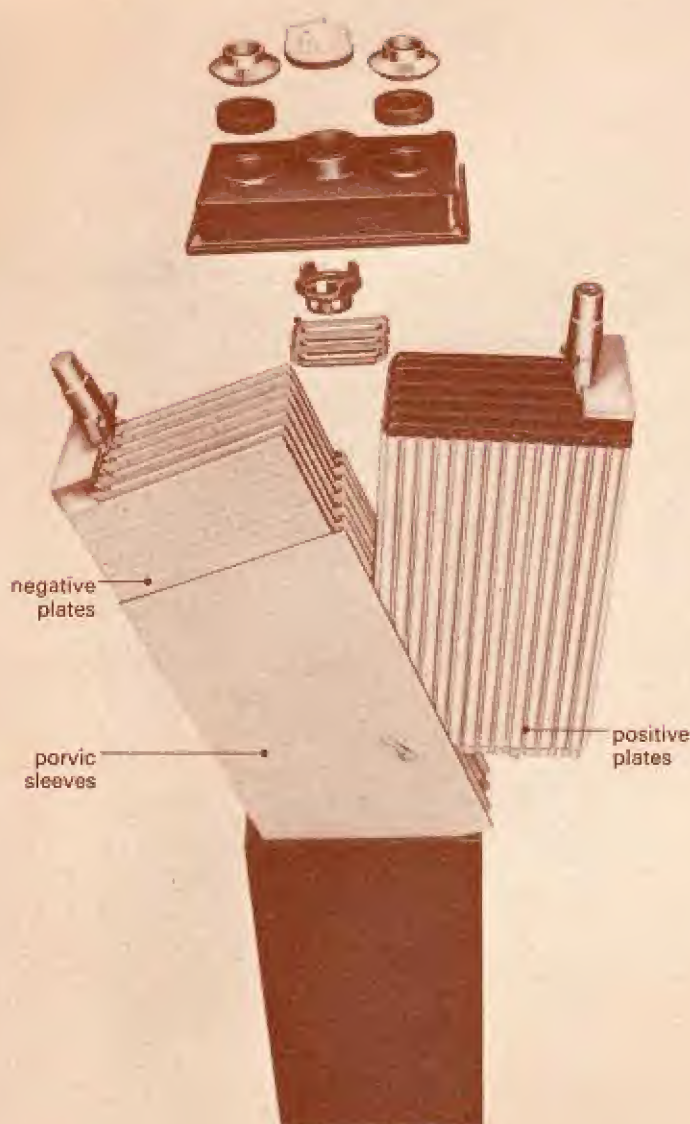
Electricity is a very difficult commodity to store. We can manufacture coal gas and store it in a gasometer for use as required but because an electric current is essentially a flow or movement of electrons we cannot hope to store electricity in any such reservoir.

The methods adopted for storage are consequently very indirect. The pumped storage scheme linked to the Trawsfynydd nuclear power station in North Wales is typical. When the output of the power station is not being fully used, for instance at night, the surplus power available is used to pump water from a low reservoir to a higher one. Then, during 'peak periods' when extra power is called for, the water is allowed to run back to the lower reservoir through a hydro-electric generating plant. The alternative method, with which we are concerned in this book, is to use storage cells or accumulators.

The lead acid accumulator - Both the electrodes of this familiar accumulator are lead. In a charged cell ready to deliver current, one plate consists of spongy lead metal and the other of a lead grid packed with lead dioxide. The plates are separated by porous insulators of wood or plastic. These insulators hold the plates apart; they do not provide compartments for two solutions. The electrolyte is 30 per cent sulphuric acid with a density of 1.22 g cm^{-3} .

A great deal is known about the construction of lead acid accumulators, about the effects of using lead-antimony and lead-cadmium alloys, about different methods of forming the electrodes, and about the influence that varying the temperature and concentration of acid has upon the performance and life of the batteries. Less is known about the actual chemical reactions occurring in the cells, although these have been frequently studied.





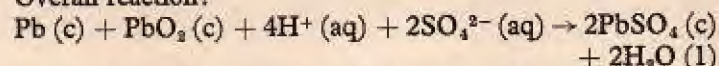
Lead sulphate is formed at both electrodes when current is drawn from the cell. The electrolyte becomes more dilute – sulphuric acid is used up in the reaction. Some very accurate experiments have been carried out and have shown that exactly 2 g-mol of sulphuric acid are used up for every 2 faradays of electricity delivered by the cell, and that 2 g-mol of water are formed.

On this basis the electrode reactions could be

1. –ve terminal $\text{Pb (c)} \rightarrow \text{Pb}^{2+} \text{ (aq)} + 2e^-$
followed by $\text{Pb}^{2+} \text{ (aq)} + \text{SO}_4^{2-} \text{ (aq)} \rightarrow \text{PbSO}_4 \text{ (c)}$
2. +ve terminal $2e^- + \text{PbO}_2 \text{ (c)} + 4\text{H}^+ \text{ (aq)} \rightarrow \text{Pb}^{2+} \text{ (aq)} + 2\text{H}_2\text{O (l)}$

followed by $\text{Pb}^{2+} \text{ (aq)} + \text{SO}_4^{2-} \text{ (aq)} \rightarrow \text{PbSO}_4 \text{ (c)}$

Overall reaction:



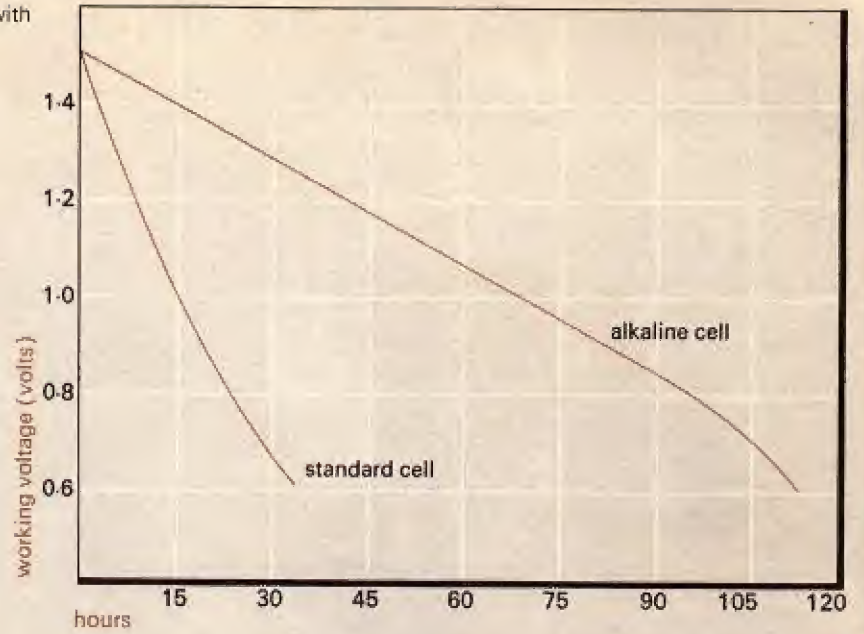
The working voltage of the cell depends on the concentration of acid, but it is usually about 2 volts, and is fairly constant during discharge.

The reverse reaction comes into operation when the cell is charged. Space is left between the plates for the sulphuric acid.

Storage cells with alkaline electrolyte – There are two equally well-known types of alkaline accumulators using nickel hydroxide.

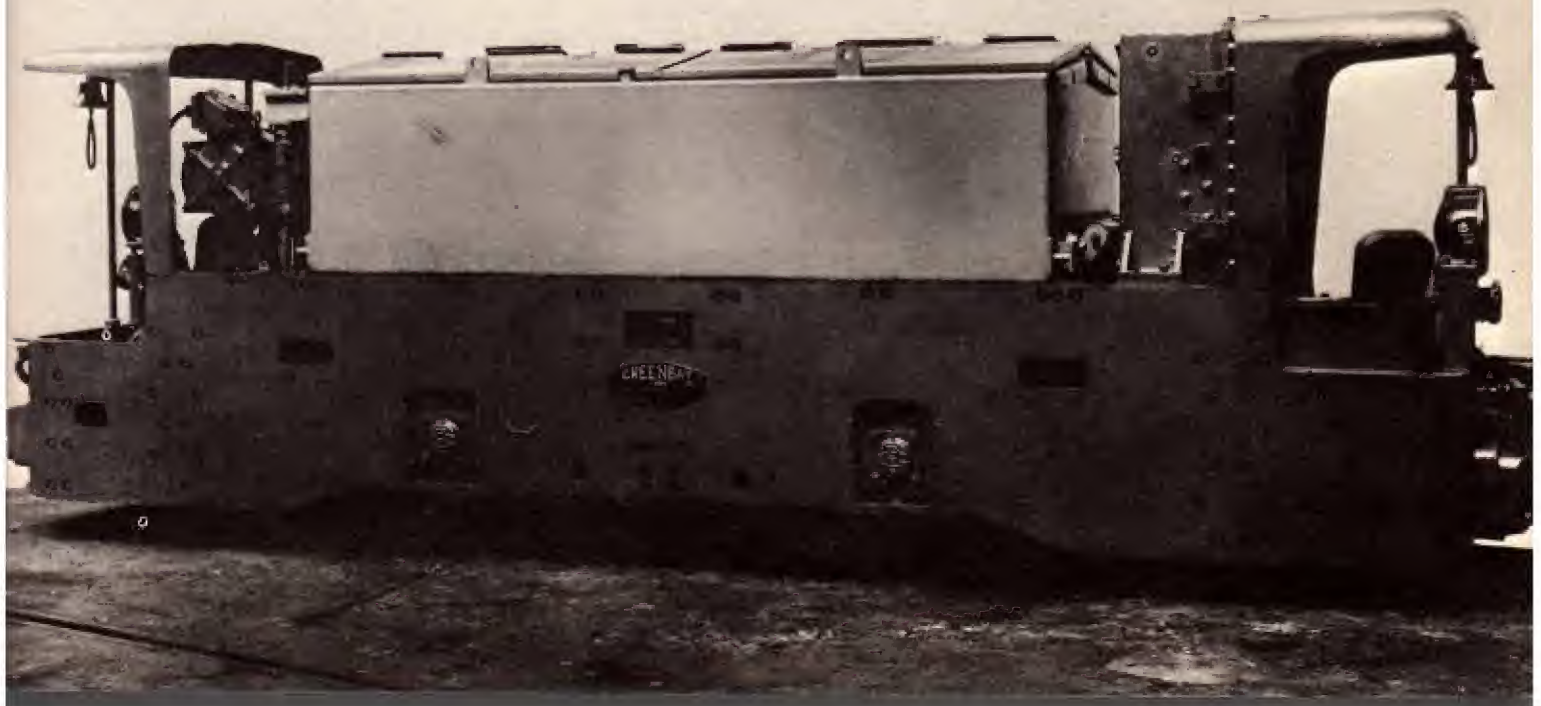
	<i>Nickel-Iron Cell</i>	<i>Nickel-Cadmium Cell</i>
Electrode 1 (positive)	Nickel hydroxide + nickel metal flakes packed into perforated steel cylinders held in a steel frame.	Nickel hydroxide + graphite packed into flat pockets of perforated steel and held in a steel grid.
Electrode 2 (negative)	Iron oxide packed into flat pockets of perforated steel and formed into a flat plate.	Cadmium oxide and iron oxide packed into flat pockets of perforated steel and formed into a flat plate.
Electrolyte	21 per cent potassium hydroxide solution.	21 per cent potassium hydroxide with a little lithium hydroxide.
Container	Steel – not attacked by alkali at this concentration.	

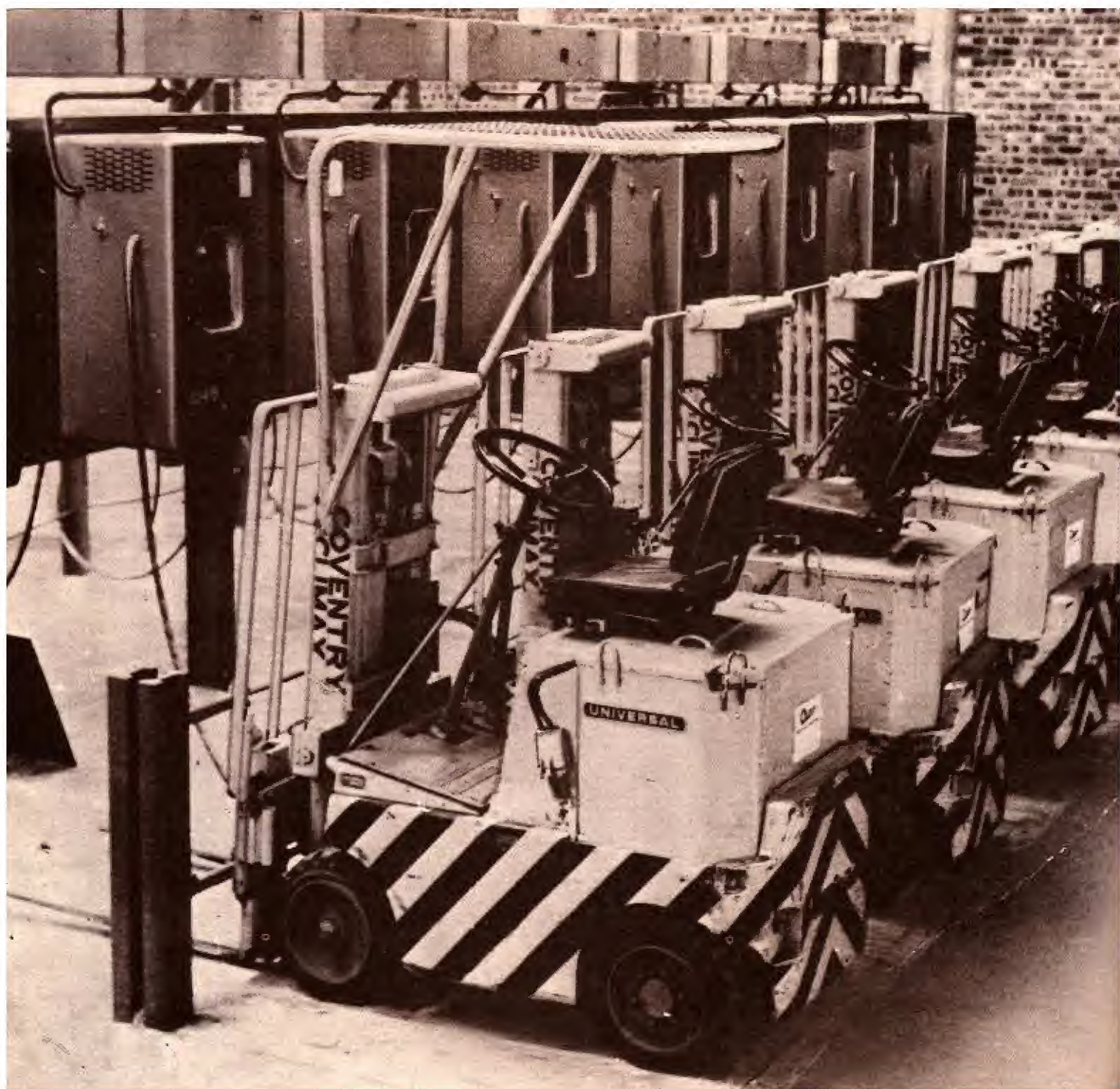
Comparison of alkaline with standard cell.



A few uses of storage batteries:

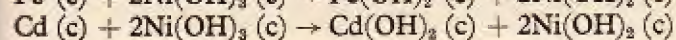
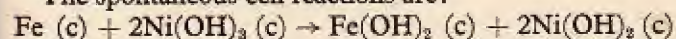
a. Battery locomotive for underground coal haulage; the battery tank is between the two driving cabs.
Greenwood and Batley Ltd.





During the initial charging of the cells the iron oxide and cadmium oxide of electrodes (2) are reduced to the metal.

The spontaneous cell reactions are:



Two faradays of electricity are transferred per gram equation. The working voltage of each cell is about 1.2 volts.

The potassium hydroxide electrolyte is not consumed in the cell reaction, so that there is no change in the volume or weight of the electrolyte during discharge. This means in turn that very little electrolyte is actually needed in the cells and the plates can be packed close together.

The capacity of a storage cell – An example of the way this factor is usually quoted is '60 ampere-hours at the 10 hour rate'. This means that the cell will deliver 60 ampere-hours if discharged in 10 hours at the minimum voltage recommended for this particular accumulator. This is 1.75 volts for a lead acid cell.

The ampere-hour method is useful because it tells us what

current we can draw from a cell in a definite time; in the above example we could draw 6 amperes for 10 hours. The electrical energy delivered is the product of voltage and ampere-hours and is measured in watt-hours (watts = volts \times amperes) and the capacities of cells are sometimes rated in these units.

The volume or weight of a cell may also be an important factor for some purposes. It is also common for capacities to be given as ampere-hours or watt-hours per lb weight or per kg.

Because we never draw all the available electricity from a storage cell before recharging it, the capacity refers to the normal output of the cell between charges and not the total quantity of electricity required to charge the cell for the first time.

c. Milk delivery vehicles.
Smith's Delivery Vehicles Ltd.



b. Fork-lift trucks; the batteries are not removed from the trucks for recharging.
Westinghouse Brake & Signal Co. Ltd.

PART 6

FUEL CELLS

It is remarkable that the dry Leclanché cell, first produced commercially about 1890, and the lead acid accumulator, produced since 1881, are still the best known and most widely used cells of their type in the world today. Improvements have brought no basic changes. What we may now say about fuel cells, however, is likely to be out of date within months; for this is a branch of electrochemical technology which is being developed intensively at present.

In any electrochemical cell we have two electrodes separated by an electrolyte; at one electrode some material is oxidized, while at the other some material is reduced. This is also true of fuel cells. What the technologists are trying to do is to produce a cell which will use up very cheap materials in a continuous process without having to be recharged at frequent intervals. Let us look very briefly at the possible economic advantages of fuel cells.

Many cells have one electrode made of zinc. As current is produced, the zinc is consumed. Zinc is quite an expensive material. A great deal of petrol and oil is consumed in mining zinc ore and in transporting it to a refinery; and much coal is then used to extract the metal from its ore. The electrical energy obtained from a cell is a small fraction of the energy used up in manufacturing the zinc metal. Clearly this is not an economical use of our natural resources. It would be far better if the petrol and coal were converted directly into electricity.

In a power station coal or oil is burnt to produce heat, which is used to generate high pressure steam to turn the turbines of the electricity generators. The sequence of energy conversion is:

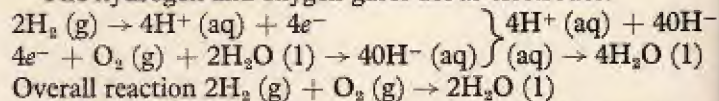
fuel \rightarrow heat \rightarrow mechanical energy (turbines) \rightarrow electricity

Because the conversion of heat to mechanical energy is

necessarily less than 100 per cent this is bound to be an inefficient sequence. In practice the efficiency is well below 50 per cent. These restrictions do not apply to the direct conversion of fuel to electricity in an electrochemical cell. In fact, high efficiencies are possible. The prospect of getting twice as much electrical energy from the same amount of fuel has naturally aroused a great deal of interest. But only recently has the fuel cell appeared to be a practical proposition.

Hydrogen-oxygen fuel cell – When water or dilute acid is electrolysed in a cell with carbon electrodes, hydrogen and oxygen gases are produced. If we stop the electrolysis while the carbon terminals are partly surrounded by the gases, we get a reverse potential and the set-up behaves as a current producing cell.

The hydrogen and oxygen gases act as electrodes.



Using our ΔG tables we can calculate that, for this reaction,

$$\Delta G = -113.38 \text{ kcal g-equation}^{-1}$$

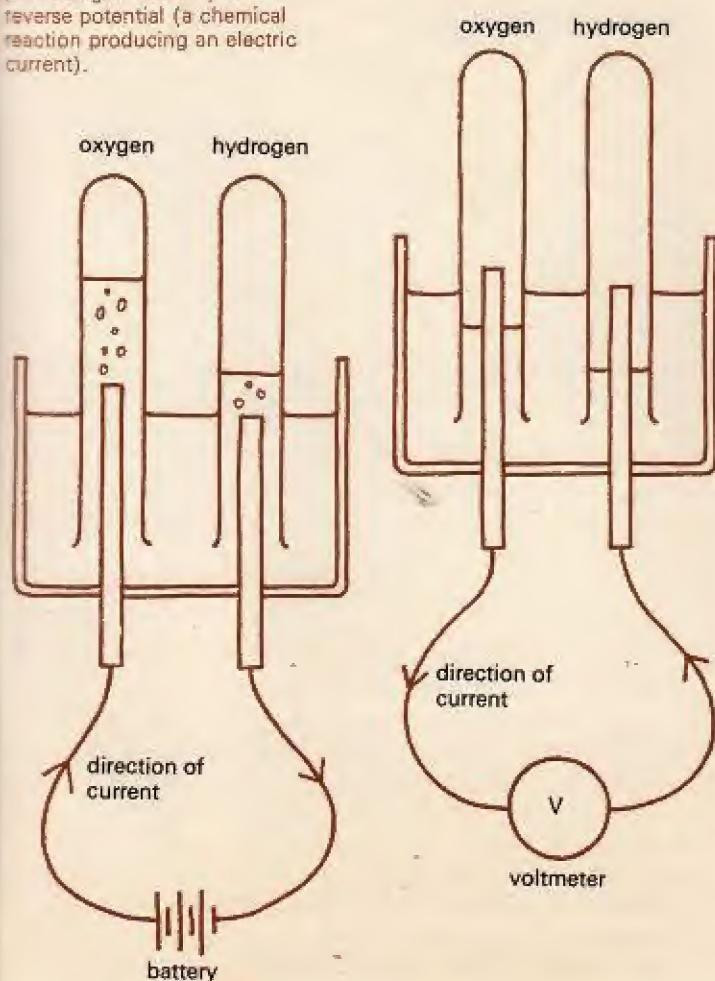
and since $\Delta G = -23 n E$ where n = number of electrons transferred in the equation = 4 $E = 1.23$ volts

We should get the same e.m.f. by bubbling the two gases from cylinders over carbon or platinum terminals. It should be noted that in the overall reaction for this cell, neither of the two carbon terminals is consumed. This is an essential feature of a fuel cell if it is to work continuously.

This experiment was first demonstrated by Sir William Grove in 1839; it was not until 1959 that a useful working cell based on this principle was built by F. T. Bacon at Cambridge.

The difficulty is that electron transfer between the gas and

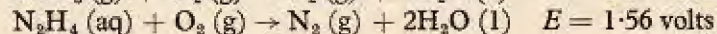
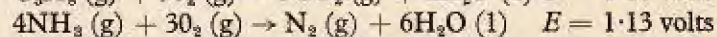
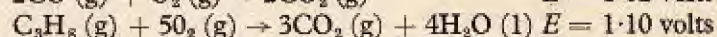
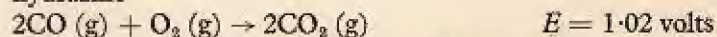
Electrolysis (an electric current producing a reaction) and reverse potential (a chemical reaction producing an electric current).



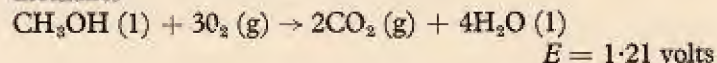
the carbon rod proceeds very slowly. It is not ordinarily possible to draw an appreciable current from the cell, since production of current requires rapid transfer of electrons. F. T. Bacon overcame these difficulties by using gases under pressure, a strongly alkaline electrolyte at 200°C , and electrodes of porous nickel which catalyse the reactions taking place on their surfaces. Bacon's cell was sufficiently powerful to operate a fork-lift truck. The use of more effective catalysts has since made it possible to operate hydrogen-oxygen fuel cells at lower temperatures and pressures. A cell of this type is being developed in the United States for the manned moon-flight project. Some of its advantages are that it operates perfectly quietly; it has no moving parts to break down; no noxious fumes are produced. Indeed, the only reaction product is water. It has been suggested that this might provide a supply of drinking water on the flight. Another project is to use mains electricity at off-peak times to electrolyse water and to store the hydrogen and oxygen produced for use in this type of fuel cell: this would be another indirect method of storing electricity.

We can calculate the theoretical e.m.f. of the cell as we did for the hydrogen-oxygen reaction, for several other simple oxidation reactions:

hydrazine

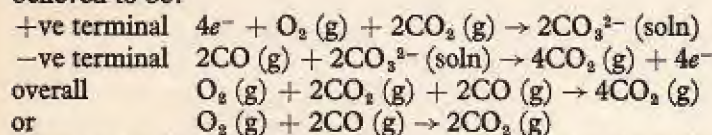


methanol

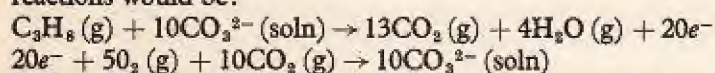


In each case we must persuade the reaction to proceed by an electrochemical path in a suitable cell, and at a reasonable rate. The last two reactions quoted – the oxidation of hydrazine and of methanol – have both been used in fairly effective practical cells, but neither fuel is particularly cheap. Hydrogen itself is another expensive fuel; the hydrogen-oxygen fuel cell suffers from the same disadvantage. Great efforts are therefore being made to find catalysts for the hydrocarbons of petrol, paraffin, and diesel oil, all of which are readily available from crude petroleum. Powdered coal has been used in some experimental cells. Attempts are also being made to find natural catalysts, or enzymes, which will allow sewage waste material to be oxidized in a fuel cell.

One way of avoiding the catalyst problem is to operate at high temperatures. Cells have been set up with electrolytes of fused sodium and lithium carbonates at 550–750° C. One such cell feeds a mixture of oxygen and carbon dioxide to one electrode and carbon monoxide to the other. The reactions are believed to be:

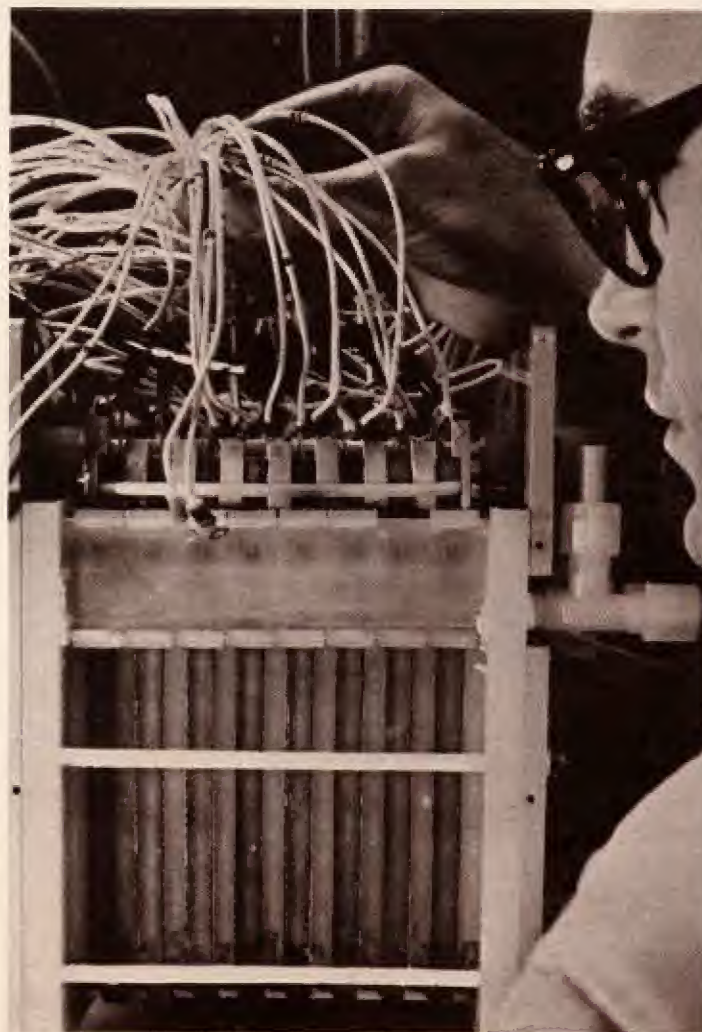


If we had a similar cell operating on propane the electrode reactions would be:



The transfer of so many electrons per gram equation is obviously very desirable, but the engineering difficulties of handling gases and fused salts at these temperatures, as well as the chemical difficulties allied with the possibility of alternative reactions, are very great. In terms of fuel economics, the energy required to heat the salt bath and keep it in a molten state may be greater than the electrical energy produced. Suitable low temperature catalysts are still to be found.

Part of a newly developed fuel cell battery which converts liquid fuel (methanol) directly into electricity.
An Esso photograph.



PART 7

USING ELECTRICITY TO PRODUCE NEW MATERIALS

In this book we have been mainly concerned with the production of electricity by electrochemical action. We have also seen how the spontaneous chemical reaction in a storage cell is driven in reverse by the application of a stronger opposing potential. In this last section we will take a quick look at some other instances where electricity is used to bring about some desired chemical reactions. Among the most important are: *a.* extraction of metals from their salts; *b.* refining of metals; *c.* electroplating; *d.* electrocleaning and electropolishing; *e.* manufacture of chemicals; *f.* anodizing.

All these applications are based upon the electrolytic cell through which electricity is driven from a source of current. The electrode which is connected to the positive terminal of the source is called the *anode*, and the one which is connected to the negative terminal of the source of current is the *cathode*.

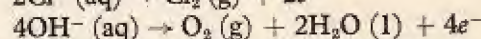
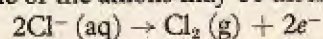
During electrolysis, positive ions (or cations) are attracted to the negative cathode. There may be several of these in the electrolyte, including H^+ (aq) if the solution is made up in water. The ion which stands lowest in the table of electrode potentials is most likely to be discharged. The table is set out with the large negative electrode potentials at the top and the large positive electrode potentials at the bottom. Thus Fe^{2+} (aq) is more likely to be discharged than Na^+ (aq), H^+ (aq) more likely than Fe^{2+} (aq), and Cu^{2+} (aq) more than H^+ (aq).

If one ion is present at a very low concentration the order may be slightly altered. If there are two ions present standing close together in the electropotential series the two may be discharged simultaneously. Furthermore, when the most likely ion has been discharged almost completely, the discharge of the next most likely ion begins. Another complication arises with hydrogen ions: at some electrodes, such as mercury, the hydrogen ion is not discharged as might be expected and other

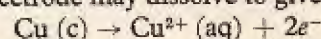
less likely ions take its place in the order of discharge. This is known as 'hydrogen overpotential' or 'overvoltage', and we shall see instances where we are able to take advantage of it.

To the positive electrode (anode), negative ions (or anions) are attracted, including OH^- (aq) in aqueous solutions. If we have a metal anode, say of copper, the discharging possibilities are these:

1. Any one of the anions may be discharged



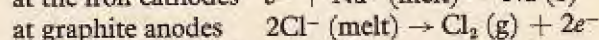
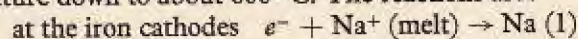
2. The metal electrode may dissolve to give ions



The most likely of these is the one that stands highest in the electropotential series. Of the three examples quoted above, hydroxyl ion discharge is more likely than chloride ion discharge, but the dissolution of the copper is more likely than either.

Extraction of metals – Let us look at the extraction of certain metals by electrolysis.

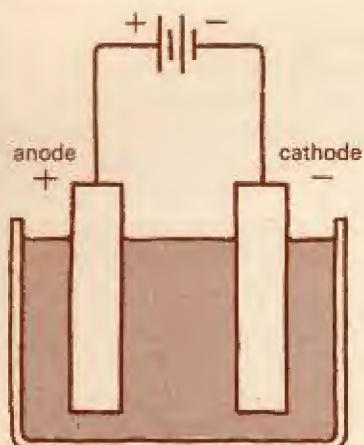
Sodium. If we electrolyse sodium chloride in aqueous solution there is no possibility that sodium ions may be discharged to produce sodium metal, because hydrogen ions are always discharged instead. Sodium is therefore produced by the electrolysis of fused sodium chloride in the Downs cell; sodium carbonate is added to bring the melting point of the mixture down to about 600°C . The reactions are:



The chlorine produced is a useful by-product of the process.

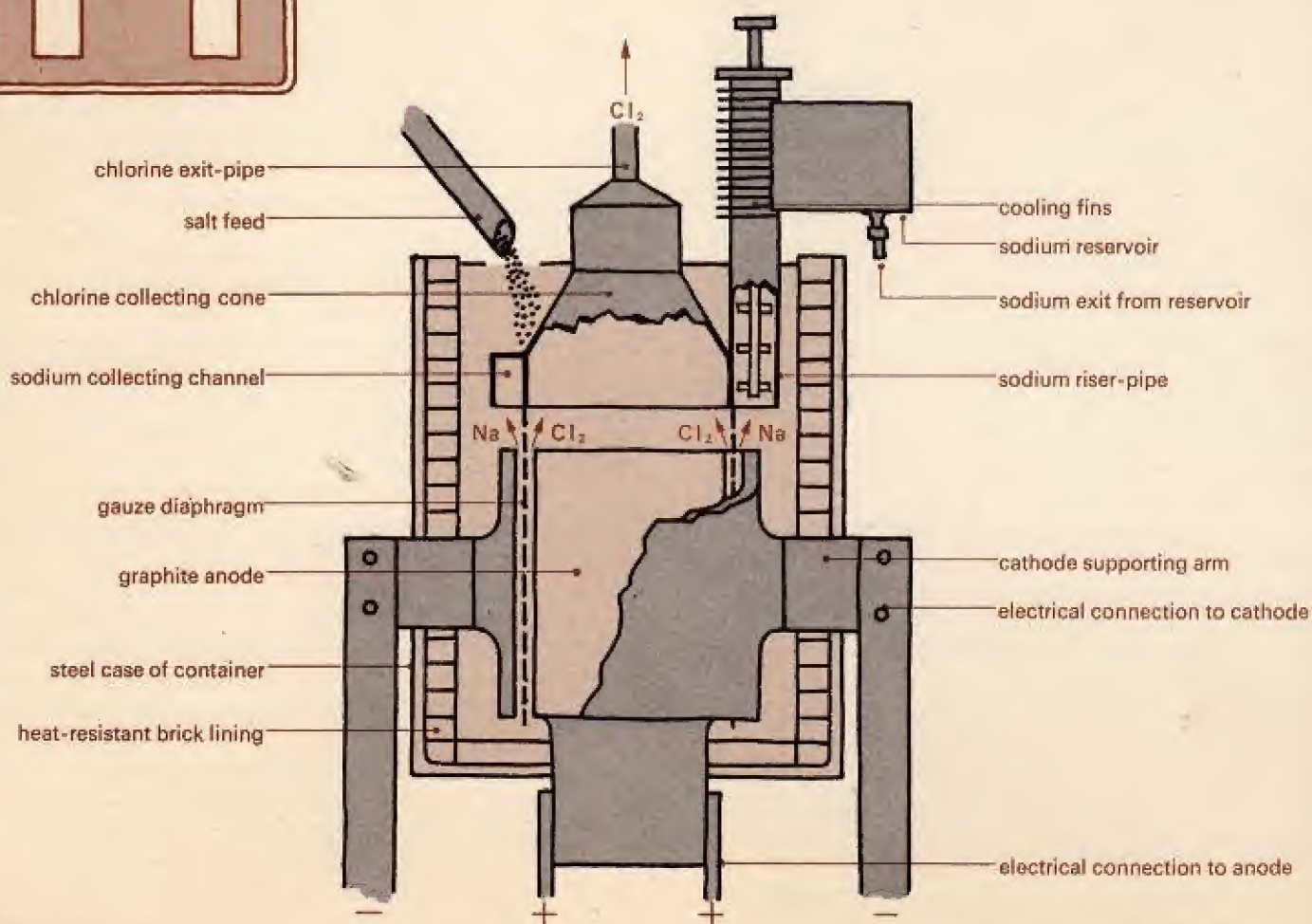
It is interesting to note that Sir Humphry Davy first isolated the alkali metal potassium by electrolysis in 1807

Electrolysis.



Downs sodium cell.
I.C.I.

Pipeline (right) which carries water to the power station of an aluminium reduction plant.
British Aluminium Company Ltd.



within seven years of Volta's discovery of the electric cell.

Aluminium is another metal which cannot be isolated by the electrolysis of its salts in aqueous solution. It can be obtained by the electrolysis of a solution of aluminium chloride in a mixture of ethyl bromide and benzene, but this is inconvenient for large-scale production. Molten aluminium chloride is a very poor conductor and aluminium oxide has a melting point of over 2000° C. Suitable working conditions are provided by a mixture of 5 per cent aluminium oxide in cryolite, which is a mineral containing sodium and aluminium

fluorides. The overall reaction at about 1000° C with carbon electrodes is:



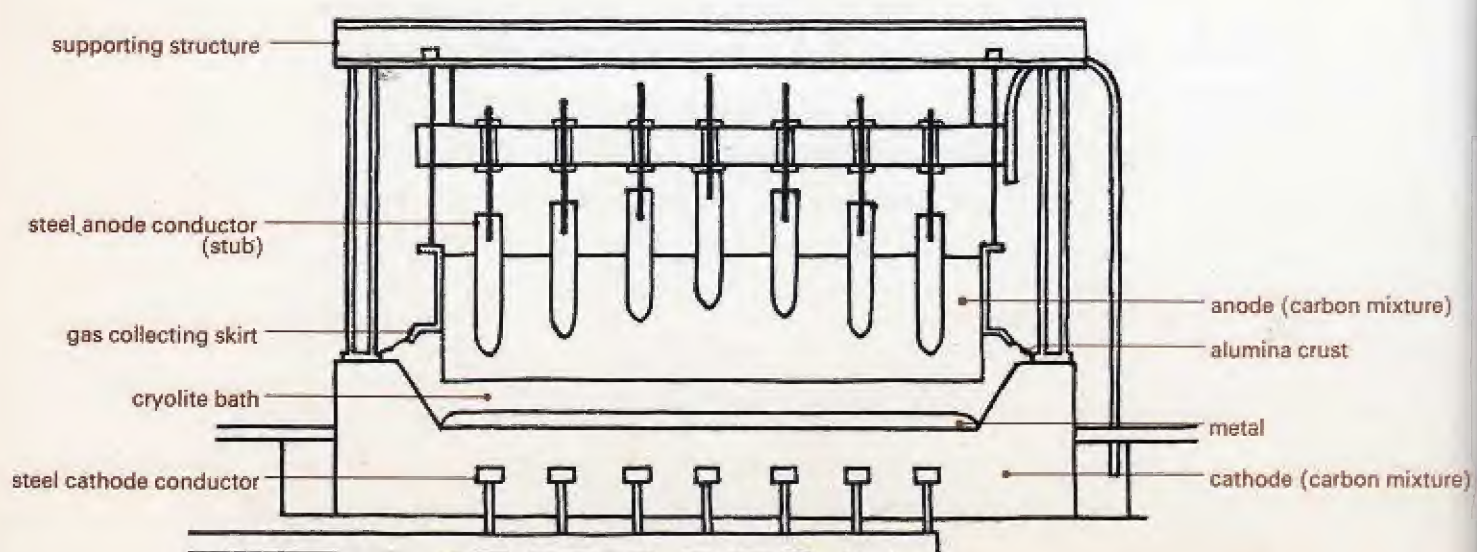
In molten solutions like this we cannot apply our standard electrode potentials, but a typical industrial cell works at 5 volts and 40,000 amp, producing some 600 lb of aluminium per day. Because of the very heavy current drain required most aluminium extraction plants have their own hydro-electric generators.

Magnesium is also extracted by electrolysis. A molten





Aluminium reduction furnace.
British Aluminium Company Ltd.



mixture of magnesium, potassium, sodium, and calcium fluorides is electrolysed.

Refining of metals – aluminium. The aluminium metal prepared by the electrolytic process is about 99.5 per cent pure, but may be refined to 99.99 per cent purity by a second electrolysis. Here again the electrolyte consists of molten salts – aluminium, sodium, and barium fluorides – in which aluminium oxide has been dissolved, at about 1000° C. The raw aluminium metal is deliberately mixed with copper and silicon so that it sinks to the bottom of the bath where it is made the anode of the cell. The cathode is a thin sheet of very pure aluminium on top of the melt. During electrolysis:

at the anode $\text{Al (raw metal)} \rightarrow \text{Al}^{3+} + 3e^{-}$

at the cathode $\text{Al}^{3+} + 3e^{-} \rightarrow \text{Al (pure metal)}$

The overall reaction is therefore the transfer of very pure aluminium from the anode to the cathode, leaving behind any impurities.

Copper is also refined by electrolysis but under much milder conditions. The electrolyte is an aqueous solution of 10 per cent copper sulphate and 20 per cent sulphuric acid at 60° C. The anodes are slabs of impure copper and the cathodes are thin sheets of very pure copper which gradually thicken during electrolysis. Silver and gold are among the impurities left behind at the anode. When enough of this anode 'slime' has accumulated the precious metals are recovered.

In the electrorefining cell we have two almost identical electrodes, copper in copper sulphate solution. A very small potential should be sufficient to bring about electrolysis. In practice the cells are operated on 0.1–0.3 volts.

Electroplating – The object of plating may be twofold. The main purpose is usually to protect the underlying metal from corrosion. An important secondary aim may be to improve the appearance of the product. A car bumper is perfectly adequately protected if it is covered with a dull layer of chromium, but it looks more attractive if it has a bright polished surface. The metals used for plating are normally expensive – chromium, silver, nickel, or tin. As little as possible is used, but the plating must be uniform without scratches or pinholes, and it must adhere to the basic metal as though it were part of it. A great deal is known about the art of electroplating: what conditions of temperature and concentration, what added substances, what currents and what voltages will give the best results. It is still very much an art, however, for the scientific

principles underlying all these variables are complex.

For chromium plating the bath usually consists of chromium(VI) oxide in very dilute sulphuric acid. The cathode in the bath is first plated with less expensive copper or nickel and then given a plating of chromium which is rarely more than 0.00002 inches thick.

Nearly all the tin-plating in this country is now done electrolytically. A continuous steel strip is drawn through a plating bath of tin salts in sulphuric acid, with several added components which have been found to improve the finished product. The strip becomes the cathode of the cell and the anodes are slabs of pure tin. The overall reaction, as in copper refining, is the transfer of pure metal from anode to cathode without change in the concentration of the bath. The strip remains in the electrolytic cell for about two seconds and a layer of tin $15\text{--}60 \times 10^{-6}$ inches thick is plated onto the steel.

Electrocleaning and electropolishing – Materials which are to be electroplated are frequently cleaned electrolytically in order to ensure that the surface is perfectly free from grease and oxide which may impair the adhesion of the plated layer to the metal. The cleaning bath may be acidic or alkaline. The object to be cleaned may be the anode or cathode, or both alternately if alternating current is used. The cleaning action may involve attack by hydroxyl ions on grease, reduction of oxides by discharged hydrogen, or scouring of the metal surface by bubbles of gas. In the continuous strip tinplating process the steel strip is cleansed five times. On arrival it is cleaned in sulphuric acid to remove steel-works scale. Then during cold rolling to the required thickness it is greased with fat or palm oil. This is removed in a one second alternating current electrolytic cleaning bath containing alkali and detergent. After annealing and temper rolling the strip is fed through an alkali cleaning bath, an electrolytic acid cleaning bath, and a water washing bath directly into the plating cell.

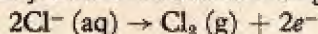
It has been found that when metals are used as anodes in certain electrolyte baths – perchloric acid for aluminium, for example, or phosphoric acid and alcohol for magnesium – the surface of the metal becomes polished. Soon no scratches remain. It is believed that the peaks on the metal surface dissolve first leaving the valleys untouched until the surface is flat. This is another useful preliminary to plating since plated layers adhere better to a polished surface.

Manufacture of chemicals – hydrogen and oxygen are produced commercially at a purity of better than 99.8 per cent by the large-scale electrolysis of 20 per cent sodium hydroxide solution. The conductance of pure water is of course too low for a current to be carried across the cell. Dilute alkali is preferred to dilute acid because the concentration does not attack the steel container of the cell. The electrodes are of steel plated with cobalt or nickel. The theoretical potential difference required to decompose water is about 1.2 volts but in practice 2 volts are required to give a useful rate of electrolysis.

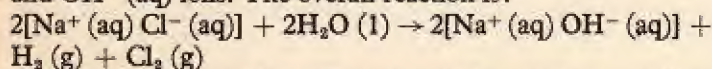
Chlorine and sodium hydroxide. The electrolysis of fused sodium chloride is used to produce sodium metal and chlorine. The electrolysis of sodium chloride solution is another important industrial process.

In one type of cell 28 per cent sodium chloride solution is electrolysed with graphite anodes and iron cathodes. A porous diaphragm is set between each pair of electrodes. The reactions are:

At graphite anodes – chlorine gas is evolved. We would expect hydroxyl ions to be discharged and oxygen gas evolved, but owing to the greater concentration of chloride ions and to the 'oxygen overpotential' (similar to hydrogen overpotential) at graphite electrodes, chloride ions are discharged in preference.

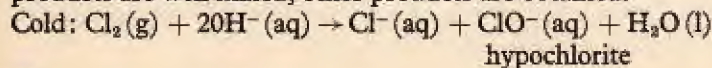


At iron cathodes – hydrogen gas is evolved as expected, hydrogen ions being more easily discharged than sodium ions. Each hydrogen ion discharged leaves behind a hydroxyl ion (from the water $\text{H}_2\text{O} (\text{l}) \rightarrow \text{H}^+ (\text{aq}) + \text{OH}^- (\text{aq})$). Thus, around the iron cathodes, we have an accumulation of $\text{Na}^+ (\text{aq})$ and $\text{OH}^- (\text{aq})$ ions. The overall reaction is:



The diaphragm in the cell prevents the resulting sodium hydroxide solution from mixing with the chlorine evolved at the anode. When the sodium hydroxide concentration has reached about 15 per cent the solution is withdrawn and evaporated. Excess sodium chloride crystallizes out first and caustic soda is eventually obtained.

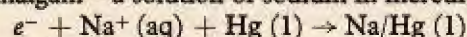
If the cell is used without a diaphragm and the reaction products are well mixed, other products are obtained.



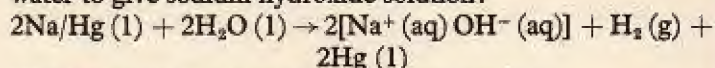
hot: further reaction to ClO_3^- – chlorate.

Both sodium hypochlorite (bleaching powder) and sodium chlorate (a weed killer) are useful products.

In a second type of cell the cathode is of mercury, and the anode is of graphite. Chlorine is evolved at the anode as before. At the mercury cathode hydrogen ions do not discharge readily. It becomes possible for the sodium ions to discharge, not as metallic sodium which would be far too reactive and would immediately decompose the water, but as sodium amalgam – a solution of sodium in mercury.

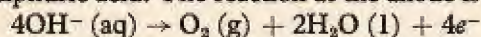


When the sodium concentration in the amalgam is about 0.2 per cent it is run off into a second cell where it reacts with water to give sodium hydroxide solution:



The hydrogen gas is again a useful by-product.

Anodizing – Aluminium is a very reactive metal; it is unsuitable for use out of doors unless covered with a protective layer of unreactive oxide. The process can be brought under control and the thickness of the protective layer increased by making the aluminium an anode in an electrolytic cell containing sulphuric acid. The reaction at the anode is:

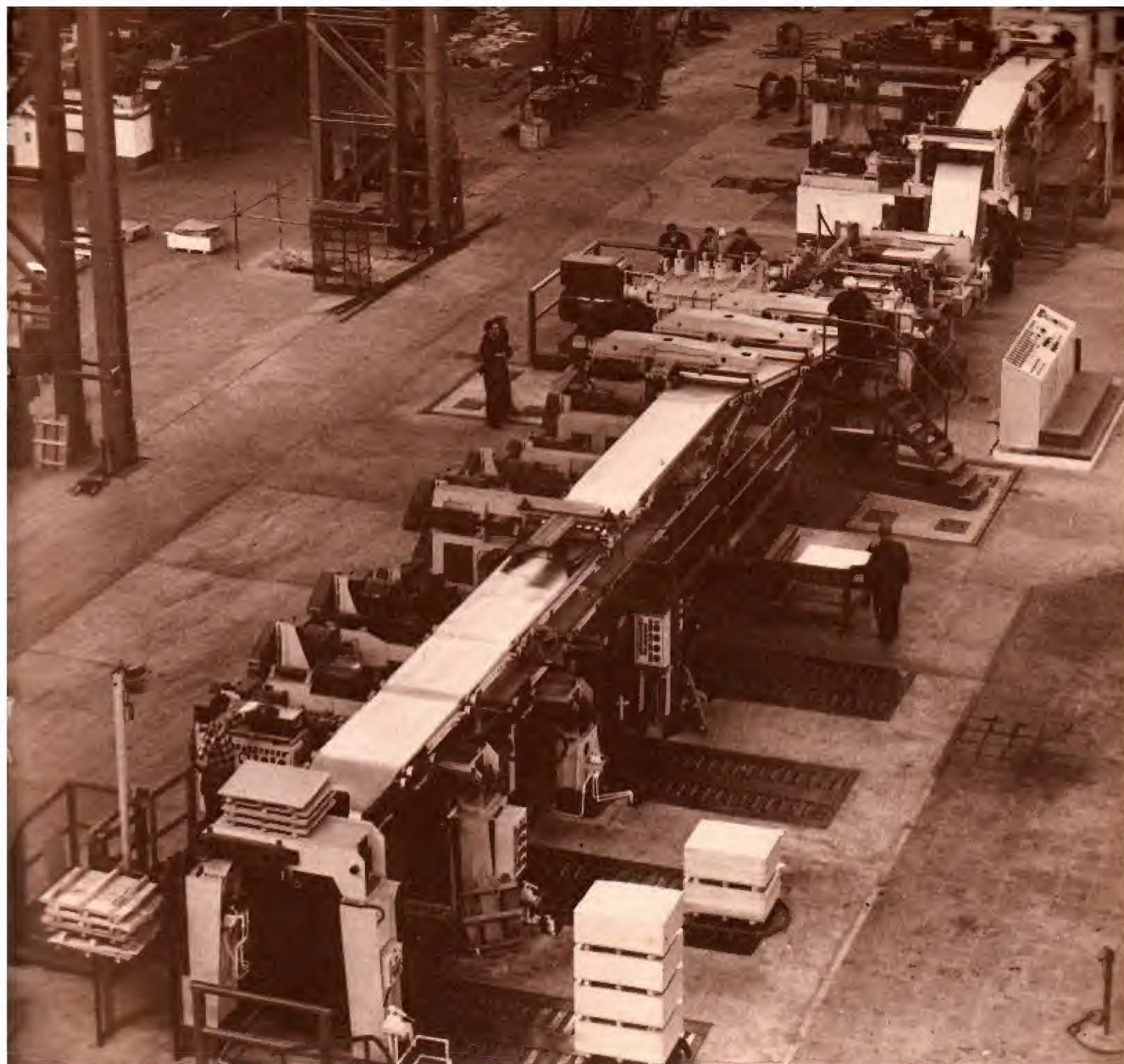


During the discharge process part of the oxygen is used up in forming a layer of oxide on the surface of the metal.

Initially this layer is rather porous and is very suitable for dyeing. If the object is immersed in a solution of a dye, the dye is absorbed into the pores of the oxide layer. If the dyed object is then transferred into boiling water the oxide is converted into a hydrated form which takes up more room than the simple oxide. As a result, the whole layer becomes sealed, dye and all, into a hard, tightly packed layer. In addition to being attractive and protective the coloured hydrated layer is a good electrical insulator. The coloured anodized finish is incorporated in a wide range of aluminium products, from ashtrays and kitchen equipment to building materials.

Aluminium alloys, magnesium, and magnesium alloys may also be anodized.

Electronic tinning line, a continuous strip electroplating process.
Steel Company of Wales.



Chemistry Background Books

General editor H P H Oliver Author of this book Dr Iolo Wyn Williams

Art editor Ivan Dodd

Published for the Nuffield Foundation by Longmans/Penguin Books

Longmans Green and Co Ltd London and Harlow

Penguin Books Ltd Harmondsworth Middlesex England

© Nuffield Foundation 1969 First published 1969

Made and printed in Great Britain by Newgate Press Limited

CBBO4344

